STUDIES ON APPLICATIONS OF CHITOSAN AND SYNTHESIZED CHITOSAN DERIVATIVES IN TEXTILE PROCESSING

A THESIS SUBMITTED TO
THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA
FOR THE AWARD OF THE DEGREE OF

DOCTOR OF PHILOSOPHY
IN
TEXTILE CHEMISTRY

BY
MILIND S. INAMDAR

UNDER THE GUIDANCE OF

Prof. (Dr.) D. P. CHATTOPADHYAY
HEAD
DEPARTMENT OF TEXTILE CHEMISTRY

Department of Textile chemistry
Faculty of Technology and Engineering
The Maharaja Sayajirao University of Baroda
Vadodara – 390 001

JANUARY - 2014

DECLARATION

I here declare that the thesis entitled ***"Studies on applications of chitosan and synthesized chitosan derivatives in textile processing"*** *which is submitted herewith to The Maharaja Sayajirao University of Baroda, Vadodara for the fulfilment of the award of the degree of* ***DOCTOR OF PHILOSOPHY IN TEXTILE CHEMISTRY*** *is the result of the work carried out by me in Textile Chemistry Department, Faculty of Technology & Engineering, The M. S. University of Baroda, under the able guidance of Dr. D. P. Chattopadhyay, Professor and Head, Department of Textile Chemistry, Faculty of Technology & Engineering, The M. S. University of Baroda, Vadodara.*

I further declare that the result of this work has not been previously submitted for any degree/ fellowship.

Place: Vadodara
Date: 28 /01/2014

(Mr. Milind S Inamdar)
Ph.D registration no: 251,
Date of registration: October 10, 2007

Department of Textile Chemistry

Faculty of Technology & Engineering
The Maharaja Sayajirao University of Baroda
Post Box No: 51, Kalabhavan, Vadodara- 390001, INDIA
Ph: (=91-0265) 2434188 Ext 210 Fax : 0265- 2423898

Ref. No. TC/___ **Date :** 28 **Jan 2014**

CERTIFICATE

*This is to certify that the thesis entitled "**Studies on applications of chitosan and synthesized chitosan derivatives in textile processing**" which is being submitted by **Mr. Milind S. Inamdar** in partial fulfillment for the award of the degree of **Doctor of Philosophy** in Textile chemistry to The Maharaja Sayajirao University of Baroda, is a record of bonafide work carried out by him under my supervision and guidance at Faculty of Technology & Engineering, Vadodara. The matter presented in this thesis has not been submitted for the award of any other degree.*

GUIDE
Prof. (Dr.) D.P. Chattopadhyay
Department of Textile Chemistry,
Faculty of Technology & Engineering
The M. S. University of Baroda,
Vadodara

HEAD
Prof. (Dr.) D.P. Chattopadhyay
Department of Textile Chemistry,
Faculty of Technology & Engineering,
The M. S. University of Baroda,
Vadodara

DEAN
Prof A.N Mishra
Faculty of Technology & Engineering
The M. S. University of Baroda,
Vadodara

DEDICATION

This work is dedicated my wife, Madhushree, and to my Textile Processing Department colleagues who supported me with ultimate love during the preparation of this dissertation

ACKNOWLEDGEMENT

I take this opportunity to express deep sense of gratitude to my guide and Head of Textile Chemistry Department, Prof. (Dr.) D.P. Chattopadhyay, under whose guidance, I have carried out this work. It is his constant encouragement, keen interest and invaluable guidance which has helped me to complete this work. His insight and critical evaluation have been of great help throughout the work. It was really a pleasing opportunity to work under his worthy guidance.

I express my deep gratitude to the management and principal of Sarvajanik college of Engineering & Technology, Surat for giving me the permission for the admission and allowing utilizing laboratories.

I am very much thankful to M/s Mafatlal Industries Ltd, Navasari; M/s Colourtex Ltd, Surat,M/s Marine Chemicals, Kochi, Kerala, M/s Mahtani Chitosan Pvt. Ltd., Veraval, Gujarat for providing for providing required fabrics, dyes and chemicals. Also many thanks to Dept. of Chemistry, S.P. University,Vallabh Vidyanagar, Dept of Metallurgy, Feculty of Tech and Engg, Vadodara, M/s SICART, Vallabh Vidyanagar, M/s Choksi Laboratories, Vadodara, M/s Pollucon laboratories Pvt Ltd, Surat and Chemical Engineering Department, SVNIT, Surat for providing the necessary testing facilities.

I am thankful to the librarians of Faculty of Tech & Engg, Vadodara and SCET, Surat and other standard publications for the information; I have drawn for literatures during preparation of this work.

I express my deep gratitude to Dr. S.B.Guha, Dr. S.S. Bhattacharya and Dr. A.K Mairal for their blessings and all the staff members and friends of Textile Chemistry Department namely Dr B.H Patel, Dr. S. R. Shah, Dr. J. N. Shah and Dr B.J. Agrawal for the assistance provided by them during this project work. I express my sincere thanks to my friends Javed Khan, Amit Halbe, Shweta, Ankur, Disant and all my friends who were directly or indirectly helpful me to complete this work.

Special thanks to Ashwin Rathod, Hintendra Patel, Shailesh Raval, Piyush Patel, Vijabhai, Mrs Yoginiben, Mrs Dulariben, Bhavasarbhai, and administrative staff of SCET , Surat and Textile Chemistry Department, Kalabhuvan, Vadodara for their help in doing this research work.

I am highly indebted to Rajabhau and Vahini, Aai and Baba, Mavasi, and Shri Goel saheb for their blessings and I express my sincere thanks to my wife for her forbearance & patience, without which this thesis would not have possible.

Finally, I thank to almighty for his blessings on me forever……..

Vadodara ***Milind S. Inamdar***

January28, 2014

LIST OF PUBLICATIONS

Research papers	
01.	D.P.Chattopadhyay and M.S.Inamdar, "Application of chitosan and its derivatives in removal of Cu(II) ions from water used in textile wet processing", *Textile Research Journal,* (ISSN Print: 0040-5175; Online: 1746- 7748) (*In press*) Published online on February 21, 2014, doi: 10.1177/0040517514523176 http://trj.sagepub.com/content/early/2014/02/20/0040517514523176 *(Peer Reviewed)*
02.	Debapriya Chattopadhyay and M.S.Inamdar, "Improvement in the properties of cotton fabric through synthesized nano chitosan application", *Indian Journal Of Fibre & Textile Research,* (ISSN 0971:0426) Vol.38, March (2013) 14-21 *(Peer Reviewed)*
03.	D.P.Chattopadhyay and M.S.Inamdar, "Studies on synthesis, characterization and viscosity behaviour of nano chitosan", *Research Journal of Engineering Sciences,* (ISSN 2278 – 9472) Vol. 1, No. 4, October (2012) 9-15 *(Peer Reviewed)*
04.	D.P.Chattopadhyay and M.S.Inamdar, "Aqueous Behaviour of Chitosan", *International Journal of Polymer Science*, (ISSN: 1687-9422, e-ISSN: 1687-9430) Vol 2010, (2010) 1-7 *(Peer Reviewed)*
05.	D.P.Chattopadhyay and M.S.Inamdar, "Studies on the Properties of Chitosan Treated Cotton Fabric", *Asian Dyer*, (ISSN 0972:9488) Vol 6, No 5, Oct (2009) 43-53

Review papers	
06.	M.S.Inamdar and D.P.Chattopadhyay, "Chitosan And Its Versatile Applications In Textile Processing", *Man Made Textile in India*, (ISSN 0377:7537) Vol XLIX, No 6, June (2006) 211-216

Paper presentation in conferences	
07.	D.P.Chattopadhyay and M.S.Inamdar, "Application of chitosan to cotton fabric: An eco-friendly approach" in 4th International Congress of Environmental Research (ICER-11) organized by Journal of Environmental Research and Development (JERAD) and Sardar Vallabhbhai National Institute of Technology (SVNIT), Surat on Dec 16, 2011
08.	D.P.Chattopadhyay and M.S.Inamdar, "Nano chitosan: Synthesis, characterization and application to cotton fabric" in The 11th Asian Textile Conference(ATC-11)[*Knowledge Convergence in Textiles for Human and Nature*] organized by The Korean Fiber Society and The Korea Society of Dyes and Finishes at EXCO, Daegu, South Korea on November 3 , 2011
09.	D.P.Chattopadhyay and M.S.Inamdar, "Biopolymeric Nanoparticles- Synthesis, characterization and application to cotton fabric" in International conference on Latest Trends in Nano-Science & Technology (ICNSNT-2011) organized by Khaja Bandanawaz College of Engineering , Gulbarga, Karnataka State, on March 28, 2011
10.	D.P.Chattopadhyay and M.S.Inamdar, "Effect of biopolymeric nano particle treatment on cotton fabric" in 2nd International conference on "Intelligent Science & Technology-Suniist" organized by Sun College of Engineering &Technology, Erachkulam, Dist. Kannayakumari (TN) on 18ThMarch 2010.
11.	D.P.Chattopadhyay and M.S.Inamdar, "Studies on Properties of Chitosan Treated Cotton Fabric" in 2nd National conference on Advances in Chemicals for Textile Polymers-Application and Quality assurance at PSG College of Technology, Coimbatore on 12 Feb 2009
12.	D. P. Chattopadhyay and M. S. Inamdar, "Synthesis of Nano Chitosan & its application to Textiles", in State level Seminar on " A small Step & Vast Universe – Nanoscience and Nanotechnology" organised by Vadodara Institute of Engineering, Kotambi, Gujarat on 23rd Feb 2013

Departmental presentation	
13.	"Studies On Applications of Chitosan And Synthesized Chitosan Derivatives In Textile Processing", Department of Textile Chemistry, Faculty of Technology & Engineering, The M.S.University of Baroda, Vadodara-390001, April 3, 2010
14.	"Studies On Applications of Chitosan And Synthesized Chitosan Derivatives In Textile Processing", Department of Textile Chemistry, Faculty of Technology & Engineering, The M.S.University of Baroda, Vadodara-390001, March 14, 2009

Citation
❖ Google Scholar Citation**: 16** (as on 20 /01/2014)

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

LIST OF ABBREVIATIONS

Abbreviation	Full form
AAS	Atomic Absorption Spectroscope
AATCC	The American Association of Textile Chemists and Colorists
AOX	Adsorbable Organic Halogen
APHA	American Public Health Association
APO	Aziridinyl Phoshine Oxide
ASTM	American Society for Testing and Materials
BI	Brightness Index
BOD	Biological Oxygen Demand
BS-EN	British Standard- European Standard
CCMS	Computer Colour Matching System
CD	Cyclodextrin
CHT	Chitosan of molecular weight 135,869
CHT-D1	Chitosan of molecular weight 285,231
CHT-D2	Chitosan of molecular weight 71,676
CHT-D3	Chitosan of molecular weight 38,733
CHT-D4	Chitosan of molecular weight 20,698
CHT-D5	Chitosan of molecular weight 11,986
CHT-MC	Chitosan of molecular weight 654,127
CHTN	Nano chitosan synthesized from CHT
C.I.	Colour Index
COD	Chemical Oxygen Demand
Conc	Concentration
CRA	Crease Recovery Angle
DAC	Degree of Deacetylation
DEAE	Diethylaminoethyl Chloride
DEAEMA	Diethyl Amino Ethyl Methacrylate
DMDHEU	Dimethylol Dihydroxy Ethylene Urea
DMF	Dimethyl Formamide

DNA	Deoxyribonucleic Acid
DMSO	Dimethyl Sulphoxide
DP	Degree of Polymerization
DQ	Degree of Quaternization
DS	Degree of Substitution
EDTA	Ethylene Diamine Tetra Acetic Acid
EPI	Ends Per Inch
FTIR	Fourier Transform Infrared
g/dL	Grams Per Decilitre
g/L	Grams Per Litre
GlcN	Glucosamine residue
GlcNAc	*N*- Acetyl Glucosamine residue
^{1}H-NMR	Proton Nuclear Magnetic Resonance
HTCC	*N*-[(2-Hydroxy-3- Trimethylammonium) Propyl] Chitosan Chloride
IS	Indian Standard
ISO	International Organization for Standardization
K/S	Kubelka Munk constant
LD	Lethal Dose
MLR	Material-to-Liquor Ratio
m/min	Meters Per Minute
mg/L	Milligrams Per Litre
mRNA	messenger Ribonucleic Acid
Mol wt	Molecular Weight
Mv	Viscosity Average Molecular Weight
N-Bu CHT	*N*-Butyl Chitosan
N-Bz CHT	*N*-Benzyl Chitosan
N-Dod CHT	*N*-Dodecyl Chitosan
N-Et CHT	*N*-Ethyl Chitosan
NMP	*N*-Methyl-2-Pyrrolidone
N-Np CHT	*N*-(1-Naphthyl) Methylene Chitosan
NTA	Nitrilo Triacetic Acid

O.D.	Optical Density or Absorbance
o.w.m.	On Weight of Material
PEG	Polyethylene Glycol
pdi	Polydispersity Index
PPI	Picks Per Inch
ppm	Parts Per Million
RO	Reverse Osmosis
rpm	Rotations Per Minute
SASMIRA	The synthetic and art silk mills research association, Mumbai, India
SDC	Society of Dyers and Colourists
sec	Seconds
SEM	Scanning Electron Microscope
SITRA	South India Textile Research Association, Coimbatore, India
TDS	Total Dissolved Solid
TMCHT	*N, N, N*-Trimethyl Chitosan Chloride
TPP	Pentasodium tripolyphosphate
THPC	Tetrakis Hydroxylmethyl Phoshonium Chloride
UF	Urea Formaldehyde Resin
WI	Whiteness Index
WHO	World Health Organization
YI	Yellowness Index

CHAPTER 1
INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

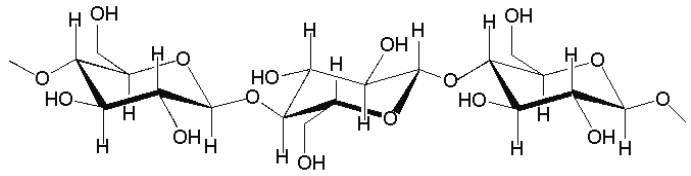
Embellishment of the cloth takes place through various unit operations of wet processing such as desizing, scouring, bleaching, dyeing, printing and finishing. To accomplish these processes, dyes and various chemicals such as acids, alkalies, oxidizing/reducing agents, electrolytes, organic solvents, surfactants, and polymers etc are used. Some of these are retained by the fabric and the excess one are discharged in one or more forms of solid, liquid and gaseous. Many of these dyes and chemicals are toxic and non-biodegradable, and hence deteriorate the ecological balance and the human health.

Ecological considerations, now days, are becoming important factors in the selection of consumer goods, all over the world. The consumers demand not only the right quality product, at right time, at a reasonable price, but also with no harm to ecology during the manufacture as well as in the use. Hence, there has been a constant urge to scientists and industrialists to explore and adopt the substitutes, that are non-hazardous and ecofriendly. The use of natural dyes on textiles has been one of the consequences of increased environmental awareness. Enzymes are commercially available for the processes like desizing, scouring, bleaching, and finishing. Eyes are, today, focused towards biopolymers to minimize the use of hazardous synthetic polymers in textile processing. Natural polymers are becoming more and more attractive as raw material for the manufacture of novelty products with wider applications in textiles, medicine and agriculture. Cellulose the commonest natural polymer is well established source for standard textiles. Others like polyaminosaccharides, alginates, starch, collagen, gelatin etc are promising naturally occurring starting materials for specialty products [1]. One such promising examples among above kind is CHITOSAN (pronounced as kite-o-san), which is derived from naturally occurring polymer CHITIN (pronounced as kite-in). Both chitin and chitosan are biopolymers and are biodegradable, biocompatible with animal and plant tissues, non toxic, and renewable [2]. Chitin, the precursor of chitosan, is a

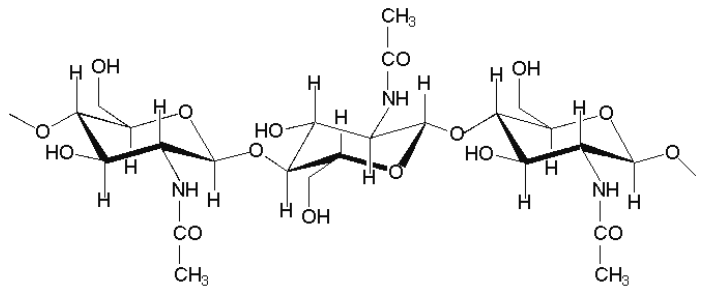
Contents of this chapter is published in:
Man Made Textile in India, Vol XLIX, No 6, June (2006) 211-216

nitrogen containing polysaccharide and is second most abundant biopolymer after cellulose. It is widely distributed in the shells of crustaceans such as crabs, shrimps, lobsters etc as well as in the exoskeleton of marine zoo-plankton, including coral, jellyfish and squid pens. It is believed that at least ten gigatons (10^{13} Kgs) of chitin are synthesized and degraded and it is also estimated that over 1,50,000 tons of chitin is available for commercial use annually [2,3].

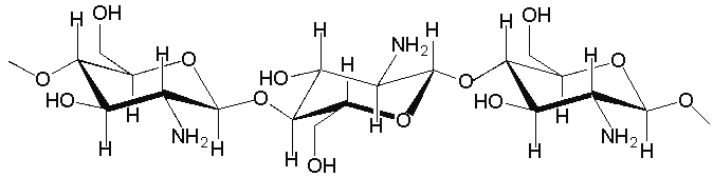
The structure of chitosan is very much close to that of cellulose except the hydroxyl group in C (2) of cellulose is being replaced by amino group in chitosan, figure 1.1. It is composed of a linear (1-4) linked 2- amino-2-deoxy-β- d- glucan (i.e. β- d-glucosamine) in the chair $^4C_1$ conformation.



Cellulose



Chitin



Chitosan

Figure 1.1 Structures of chitin, chitosan and cellulose

Chitosan, due to polycationic nature, is soluble in acidic medium and has gained enormous interest for its unique properties such as biodegradability, biocompatibility with animal and plant tissues, non toxic nature, anti bacterial, anti fungal, anti viral, anti

acid, anti ulcer, non toxic, non allergenic etc as well as film formation, fibre formation, bead formation, hydrogel formation etc. By virtue of these properties, chitosan has prospective applications in many fields such as medical, water treatment, cosmetics, dentifrices, food and textile industries. In textiles it can be in primary production of fibres, textile auxiliary chemicals and finishing agents [2-5].

Keeping in mind many valuable inherent properties and huge application potential of chitosan, the aim of present study was focused on the applications of chitosan and its various derivatives in textile processing. The work was divided into four major areas:

(1) Synthesis of chitosan of different molecular weights and determination of effect of their applications on cotton fabric,

(2) Synthesis of nano chitosan colloids and determination of effect of their applications on various properties of cotton fabric,

(3) Synthesis of *N*-substituted chitosan derivatives and determination of effect of their applications on important properties of cotton fabric, and

(4) Use of chitosan derivatives in the removal of metal ions from feed and drain water of textile processing.

Reporting of the work in this thesis comprises six chapters. Chapter 1 deals with the extensive literature survey and aims of the work. The available literature regarding applications of chitosan on textiles is reviewed in the introductory part of chapter 2 and the literature regarding nano chitosan, chemical modification of chitosan and water treatment is critically reviewed in the initial part of the chapters 3, 4 and 5 respectively.

Chapter 2 deals with the synthesis**,** stabilization and characterization of chitosans of different molecular weights, synthesized by hydrolytic degradation of high molecular weight chitosan using nitrous acid and subsequent applications of these chitosans on cotton fabrics. The molecular weights of chitosans were determined viscometrically using Ubbelohde capillary viscometer and Mark-Houwink equation. The viscosity behaviour of the synthesized chitosans was studied in presence and absence of electrolyte. The characterization of varying molecular weight chitosans was performed by analysis of FTIR spectra. The degree of deacetylation (DAC) was verified by ^{1}HNMR spectrum and elemental analysis. The effects of applications of chitosan on dyeing and finishing properties of cotton were analyzed. Chitosans of varying molecular weights and

concentrations were applied onto cotton fabric by conventional pad-dry cure method. The surface morphology of treated fabric was examined under scanning electron microscope (SEM). Effect of such treatments on physical properties like looks (in terms of whiteness, yellowness and brightness), stiffness, strength and water absorbency were examined. The chitosan was applied before and after dyeing of cotton, with direct dye and its effect on dyeing properties was examined. The effect of chitosan pre- treatment on the dyeability towards acid dyes was also investigated. The effect of chitosan on crease antibacterial resistance of cotton was also examined.

The very large molecular size and consequently high viscosity of chitosan restricts its penetration into the fibre and fabric structure and leads to only surface deposition. The surface deposition of this high polymer affects the feel and appearance of the treated textiles. This may also leads to maximum accumulation of dye on surface thereby reducing the all round fastness properties especially washing, rubbing and light fastness. In order to sustain the inherent cotton feel with improved performance, the particle size was reduced to nano level for the enhanced surface area, greater penetration in to fibre structure and efficacy of chitosan. In chapter 3, investigations relating to the synthesis, characterization and applications of nano-chitosan on textiles are reported. Nano chitosan dispersions were prepared by gel ionization technique through the reaction between chitosan and pentasodium tripolyphosphate (TPP) in aqueous medium. The samples were characterized by particle size analysis. Effect of various parameters such as molecular weight & concentration of chitosan, concentrations of TPP on particle size were determined. Attempts were made to correlate the viscosity behaviour with particle size of chitosan. The synthesized nano-chitosan was applied to cotton fabric and subsequently various properties of the treated fabric like appearance, absorbency, stiffness, dyeing behaviour, wrinkle recovery, resistance to microbial attack etc were examined. The fabric samples were pretreated with normal and nano chitosan solutions by pad-dry cure technique. The surface morphology of the nano chitosan treated cotton fabric was examined by SEM analysis.

The study reported in Chapter 4 is mainly emphasized on synthesizing a series of chitosan derivatives belonging to *N*-substituted quaternary salts having enhanced hydrophilicity and expected freedom from chlorine retention problem. Trimethyl chitosan

chloride (TMCHT) was synthesized by the reaction of chitosan (CHT) with methyl iodide in alkaline medium followed by ion exchange with sodium chloride. Further, *N*- alkyl and *N*-Aryl substituted chitosans of varying molecular size of substituents were synthesized through the reductive amination of Schiff's base obtained by the reaction of chitosan with respective aldehydes. The quaternization of *N*- substituted derivatives were then performed by the reaction of these compounds with methyl iodide as carried out for the synthesis of TMCHT. The chosen *N*-Alkyl chitosan derivates were *N*-ethyl chitosan (N-Et CHT), *N*-butyl chitosan (N-Bu CHT) and *N*-dodecyl chitosan (N-Dod CHT). For *N*-Aryl substituents *N*-benzyl chitosan (N-Bz CHT) and *N*-(1-naphthyl) methylene chitosan (N-Np CHT) derivatives were chosen. These *N*-substituted chitosan derivatives were subsequently quaternized using methyl iodide in alkaline medium. The synthesized chitosan derivatives were characterized by FTIR spectroscopy, ^{1}HNMR spectroscopy, Elemental (CHN) analysis and conductometry. Various reaction parameter variables like methyl iodide concentration, alkali concentration and the role of co-solvent (NMP) on the degree of quaternization of chitosan were studied. The effect of chain length/molecular weight of alkyl groups and molecular size of *N*-aryl substituent on the degree of substitution (DS) of CHT and degree of quaternization (DQ) of *N*- substituted CHT derivatives were investigated. The aqueous behaviour of these CHT derivatives was also studied through viscometry.

Effects of applying varying concentrations of *N*-substituted chitosan derivatives on appearance, feel, dyeing behaviour, chlorine retention, absorbency and dyeing behaviour of cotton were studied. The performance of CHT derivatives on cotton fabric was also examined for various aesthetics and value additions such as wrinkle recovery, soil release and antimicrobial properties.

Chapter 5 deals with the study associated with the application potential of chitosan and its derivatives for the recovery of valuable metals or the treatment of contaminated effluents. This research investigation was focused at understanding the chelation property of chitosan of varying molecular weights and trimethyl chitosan chloride. The study was primarily performed on chelation of calcium ions (Ca^{++}) for its ease of analysis. Study included the effect of molecular weight of chitosan, effect of concentration and kinetic on chelation. The chelation behaviour of nano chitosan

dispersion was also investigated. Similar study was conducted with copper ions. Besides volumetric analysis, gravimetric analysis and flame atomic mass spectroscopy were employed for characterization. Due to presence of hydroxyl and amino functional groups, chitosan has high affinity for different classes of dyes. The efficiency of chitosan in regard to the removal of acid and direct dyes was also determined.

Conclusions and future prospects are summarized in chapter 6.

1.2 HISTORICAL BACKGROUND OF CHITIN AND CHITOSAN

Prof. Henri Braconot, Director of Botanical Garden in Nancy (France) in 1811, first isolated a fibrous substance from the cell walls of mushroom, which he called FUNGINE. He further observed that this substance did not dissolve in aqueous acidic solutions, e.g. sulfuric acid. Later in 1823, Odier discovered that this compound is also one of the major constituent of the exoskeleton of insects and then he renamed as CHITIN (from Greek *khitōn* meaning tunic or envelope). Prof. C. Rouget in 1859, prepared a compound from chitin by treatment with concentrated caustic solution and observed that, unlike chitin, the resulting substance dissolved in acids. This compound was then named as CHITOSAN by Hoppe- Seiler in 1894 [3]. In the mean time, in 1878, Ledderhose proposed chitin to be made of glucosamine and acetic acid. However, the existence of chitosan in nature was discovered in 1954 in the yeast Phycomyces blakesleeanus.

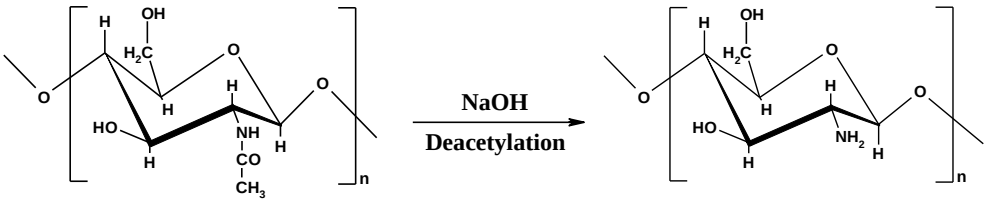
During 1930's and 1940's, researchers in Korea, Japan, Europe and USA have tested chitin and chitosan in biomedical applications. In Japan, chitosan was first used for waste water treatment to absorb grease, oils, heavy metals and other potentially toxic substances. Researchers claim that a tooth paste made from crab's shell could cut dental infections and reduce the number of visits to dentists [3, 6]. During 1970's the interest in these bio-macromolecules resulted in the first ever Chitin-Chitosan conference being held in the United States in 1977. Pioneering work of Muzzarelli during 1980's has greatly advanced our understanding of these materials [2, 3].

Chitosan has been approved as a food additive in Korea and Japan since 1995 and 1983, respectively, and thus considerable attention has given to the use of chitosan as a natural preservative to improve the shelf-life of food [7]. In the United States, the food

and drug administration (FDA) has approved chitosan for fruit juice clarification, protein recovery from food process waste, edible coatings, and as an additive for animal feed [8-10].

1.3. CHEMISTRY OF CHITIN AND CHITOSAN

Chitosan [$(C_6H_{11}O_4N)_n$] is a polysaccharide composed of a linear (1-4) linked 2-amino-2-deoxy-β- d- glucan (i.e. β- d-glucosamine) in the chair $^4C_1$ conformation. It is derived by alkaline deacetylation of chitin i.e. (1-4) linked 2-acetaamido-2-deoxy-β- d-glucan (i.e. *N*-acetyl- β- d-glucosamine), scheme 1.1. Chitin when boiled with highly concentrated sodium hydroxide solution; deacetylation takes place producing chitosan having free amino groups and sodium acetate as byproduct. The mechanism of deacetylation is similar to alkali hydrolysis acid amides [11]. In highly alkaline medium, the hydroxyl ions of sodium hydroxide (OH^-) attack the electron deficient carbonyl carbon of acetamide group on chitin to form an intermediate anion. Chain scission follows and release free amino group on main chain with liberation of acetic acid. The liberated acid then gets neutralized with sodium hydroxide. The overall reaction mechanism is illustrated in scheme 1.2.

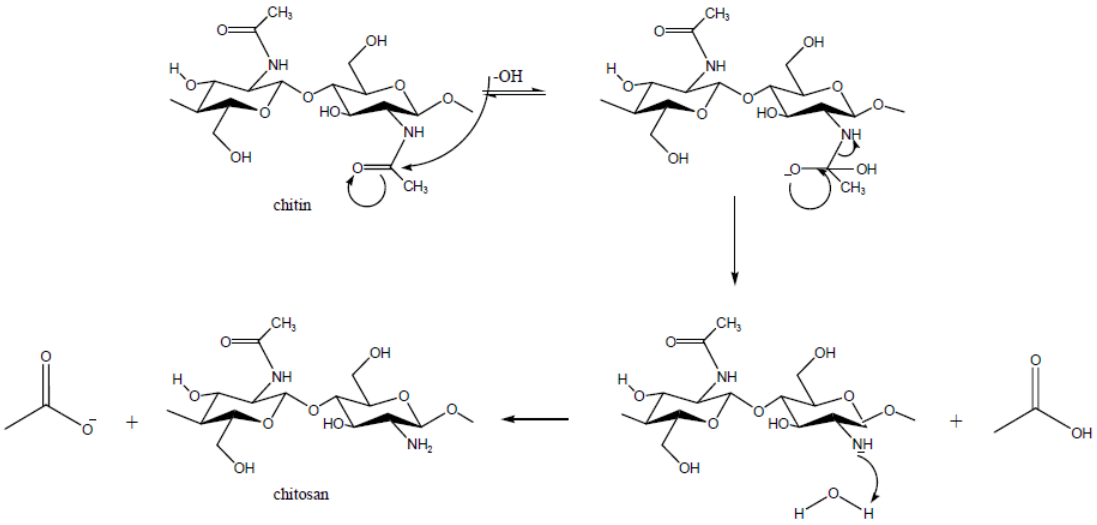


Chitin **Chitosan**

Scheme 1.1 Synthesis of chitosan by deacetylation of chitin

Between chitin and chitosan, a number of derivatives of partially *N*-acetylated chitosans exist, which is characterized by degree of deacetylation (DAC). Degree of deacetylation has a direct impact on the secondary structure of the polymeric chain and can also influence the solubility of the polymer in organic or aqueous solvents. As an evolved nomenclature, chitineous substances that do not dissolve in dilute organic acids, e.g. 1-2% acetic acid, are collectively called 'chitin'. On the other hand, chitineous

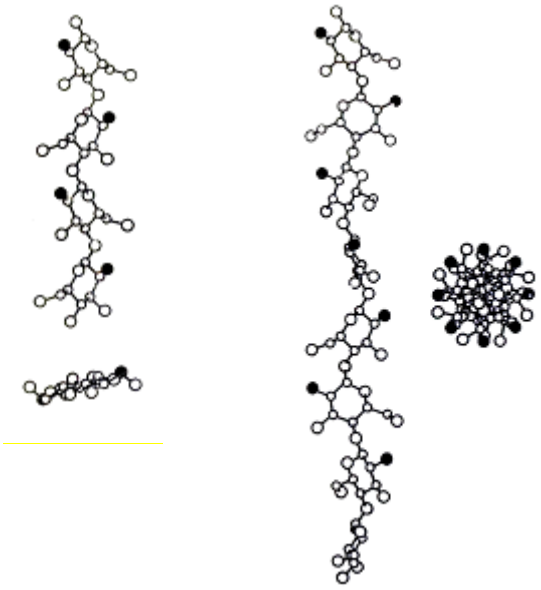
substances that can dissolve in aqueous dilute acids are referred as chitosan, approximately 60 % or above deacetylated products fall in this category. Indeed, it is a copolymer of *N*-acetyl-glucosamine and glucosamine units. The structure of chitosan is very much close to that of cellulose except the hydroxyl group in C (2) of cellulose is being replaced by amino group in chitosan, Figure 1.1 [12-19].



Scheme 1.2 Reaction mechanism of deacetylation of chitin

Chitin occurs naturally as one of three crystalline polymorphic forms, known as *α*-, *β*-, and *γ*-chitin. The chains of *α*-chitin are antiparallel but the *β*-chitin has a parallel stack structure. The *γ*-chitin form has not been fully classified but an arrangement of two parallel chains and one antiparallel chain has been suggested. Although both *α*- and *β*-chitins possess C=O·····H−N intermolecular hydrogen bonds, the *β*-chitin does not have the intermolecular hydrogen bonds between $-CH_2OH$ groups, which are present in the *α*-chitin. This fact makes it easy for the *β*-chitin to swell in water to produce hydrates unlike the *α*-chitin, which has a strong three-dimensional hydrogen bond network. The *α*-chitin is the most abundant and found in crustaceans, insects, and fungi, while the occurrence of *β*-chitin is less common and it is found in squid pens. Chitosan mainly occurs in two molecular conformations, namely (i) as extended two-fold helix and (ii) as extended eight-fold helix (Figure 1.2). The eight fold helix conformation transforms into two-fold helix under high humidity. No ordered conformation, however, is present in the aqueous

acidic solution. The molecular flexibility increases with increase in deacetylation, increase in ionic strength in the solution and increase in temperature. Chitosan is characterized by another feature, namely, the molecular weight which governs the viscosity behaviour. The average molecular weight determined by the viscosity measurement methods is of the order of $7x10^5$. The degree of acetylation of chitosan may be determined by C**:**N ratio (by elemental analysis) , ^{13}C NMR, ^{15}N NMR, by I.R. Spectroscopy, colloidal titration and gas chromatography. The molecular weights are mainly determined by viscosity measurements, light scattering spectrophotometry and gel permeation chromatography (GPC) [2, 3, 12]. The chitosan molecule is rather stiff, less than DNA and more than polyacrylate; increasing degree of acetylation value lead to a more extended conformation and stiffer chain [20].



(a) Two fold helix (b) Eight fold helix

Figure 1.2 Molecular conformation of chitosan at the solid state: (a) two fold helix conformation with side view(above) and a sectional view (below), (b) eight fold helix conformation with side view(left) and a sectional view (right)

1.4 PRODUCTION OF CHITIN AND CHITOSAN

Chitin, the precursor of chitosan, is a nitrogen containing polysaccharide and is second most abundant biopolymer after cellulose. It is widely distributed in the shells of crustaceans such as crabs, shrimps, lobsters, prawns, squilla etc as well as in the

exoskeleton of marine zoo-plankton, including coral, jellyfish and squid pens. About 20-40% chitin is present the exoskeleton of these animals. It is also present in smaller quantities in insects such as butter flies ladybugs, and the cell walls of yeast, mushrooms and other fungi, Figure 1.3. But since the crustacean shells are waste products (now byproducts) of food industry, these are commercially employed for production of chitin and chitosan [2, 3, 21]. Squid pens are also the potential source of chitin and chitosan. Squid-pens are removed from the squid during processing and are currently regarded as 'waste' so the raw material is cheap. Since, the squid pens are very low in calcium; the acid extraction step is not required. This intern reduces the cost and acid hydrolysis of chitin [22]. Therefore, comparatively cheaper and better quality chitin can be produced**.** It is believed that at least ten gigatons (10 X 10^9 T) of chitin are synthesized and degraded and it is also estimated that over 150,000 tons of chitin is available for commercial use annually. In India, it is estimated that more than one lakh tons of shrimp processing waste is being disposed annually which would be gainfully utilized for the manufacturing of chitin. Another raw material for chitin is squilla. It is estimated that a potential of around 50,000 tons of squilla is available of which nearly 5000 tons is being thrown back into the sea. This is an important trawl by catch especially in Mangalore (Karnataka) and could be used for chitin /chitosan production. The estimated availability of crab shell is about 40,000 tons in Indian waters. The average distribution of chitin in shells of various living species is listed in Table 1.1 [3].

Chitosan can directly be isolated from some fungi, mainly, Phycomyces blakesleeanus (yeast), Zygomycetes (fungus) etc species. However, the yield is too low [6, 23]. Deacetylation of chitin can also be done enzymatically. Powdered chitin is treated with *N*-deacetylase (EC 3.5.1.41) or with microbes which secrete *N*-deacetylase. The enzymatic method yields chitosan with low degree of *N*-acetylation and low degree of polymerization [24, 25]. To-date, chitosans have been produced commercially by the alkaline deacetylation of crustaceans chitins [22, 26-28].

The crustacean shells mainly consist of chitin (20-30%), proteins (30-40%), Calcium Carbonate (30-50%), lipids and traces of pigment. The dried/wet shells washed thoroughly to make it free from sand extraneous matter so as to reduce the ash content of

final product to less than 2%. The material is then crushed into a pulverous powder to help make a greater surface area available for the heterogeneous processes to follow.

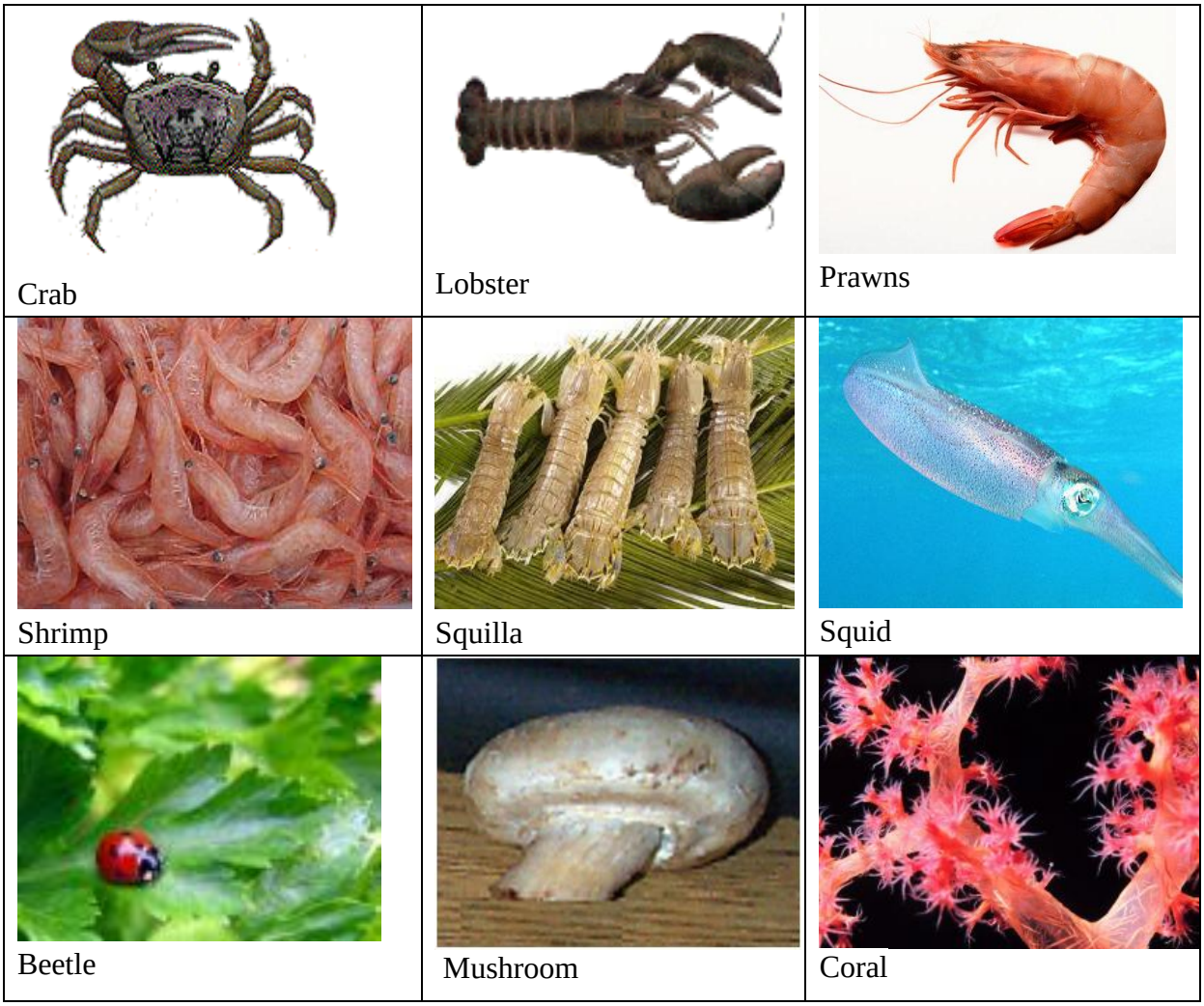


Figure 1.3 Sources of chitin

The proteins are removed by treatment with sodium hydroxide solution (5%) at about 85^{o} C to 100^{o} C for 30 minutes in a stainless steel vessal or digested enzymatically by proteases or micro-organism. The boiled raw material is allowed to cool and is then washed to with water to remove all the traces of alkali. The deproteinised shells are transferred to a mild steel vessel lined with fiber glass and is treated with hydrochloric acid (3 %) at room temperature to remove calcium carbonate. The excess acid is decanted and the residue is washed till the pH is neutral. Excess water is removed using a screw press and the dried. Lipids are extracted by soaking in organic solvents such as acetone or

ethanol. An oxidative bleaching treatment with hydrogen peroxide or sodium hypochlorite is also given to obtain a white chitin powder.

Table 1.1 Chitin content in shells of living species

Species	*** Chitin content, %**
Crustaceans	
Crab	15-35
Shrimp	14-27
Squilla	15
Insects	
Cockroach	10
Beetle	5-15
Mollusks	
Krill	40
Oyster shell	4
Squid pen	41
Microorganisms	
Aspergillus niger	42
Lactarius vellereus (Mashroom)	19
Saccharomyces cerevisiae (baker's yeast)	2.9

**On dry body weight*

Conversion of chitin into chitosan involves the deacetylation process, which is a harsh treatment usually performed with concentrated sodium hydroxide solution. Chitin flakes are treated in suspension with aqueous 40- 50 % caustic solution at 80 – 120 ^{0}C with constant stirring for 4 - 6 hours and this treatment is repeated for once or more times for obtaining high amino content product. To avoid depolymerization due to oxidation, sodium borohydrate is added**.** Excess alkali is drained off and the mixture is washed with water several times till it is free from alkali. Most of the alkali is then used either in deproteinisation or in deacetylation. Excess water is removed in screw press and the wet chitosan cake is either sun dried or in drier at 60 ^{0}C. Chitosan thus obtained is in the form of flakes and can be pulverised to powder. The flow chart for the manufacturing of chitosan from the starting material (crustacean shells) is shown in Figure 1.4.

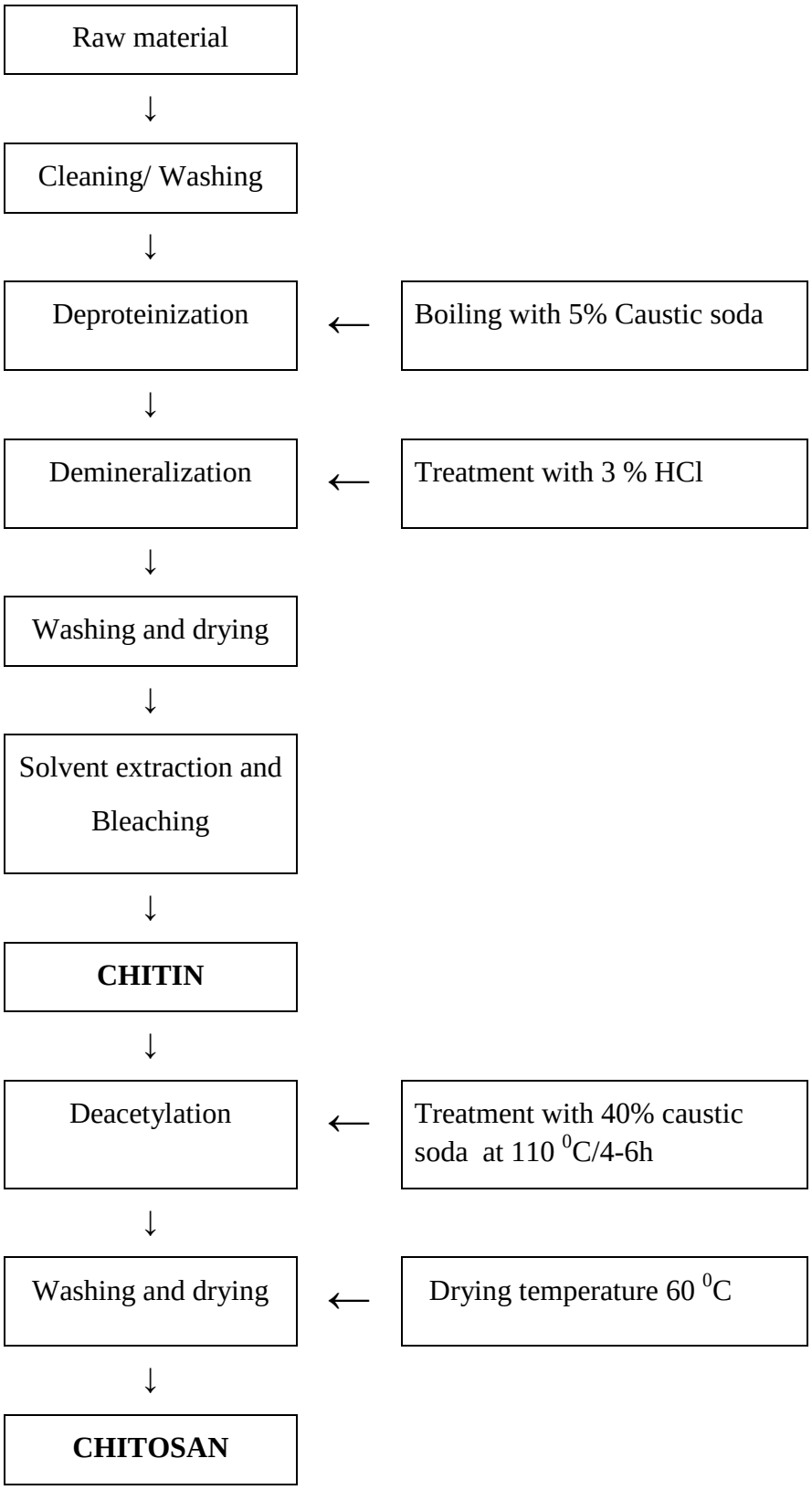


Figure 1.4 Flow chart for the manufacturing of chitin and chitosan

Alternatively, if isolation of chitin is not desired, the acid-base sequence may be reversed to directly produce chitosan.

1.5 PHYSICAL PROPERTIES OF CHITOSAN

Chitosan is a white fibrous material produced in different grades such as fibres, beads and membranes. The physical properties of chitosan are governed, at large, by two factors; the degree of deacetylation (DAC) and the molecular weight.Various factors such as source of chitin and processing parameters deacetylation determine the grades of chitosan. Chitosan being a primary aliphatic amine, it can be protonated by selected acids (p^{ka} of chitosan= 6.3). It is insoluble in water, organic solvents and alkalies, but is soluble in organic acid solutions. Structural characterization of chitosan concerning to various spectral analysis and viscometry is discussed in chapter 2 and physical properties are discussed below.

1.5.1 Colour of chitin and chitosan

The typical yellowish to brownish colour of chitin and chitosan (if not bleached) is mainly associated with the carotenoid pigment composed of astaxanthin. The carotenoids are strongly bound with proteins in the epithelial layer of the exoskeleton of chitin. The carotenoid level in crustacean is very low and varies depending on dietary pigment availability, crustacean size, its maturation, and genetic differences. The average values of pigment concentration found in the shell waste from crab, shrimp and Louisiana crawfish were estimated as 139, 147 and 108 ppm, respectively. This undesired colour can be destroyed by bleaching with hydrogen peroxide or sodium hypochlorite or by chemicking followed by peroxide bleach [28-30].

1.5.2 Degree of deacetylation

The deacetylation process involves the removal of acetyl groups from chitin molecules. The degree of deacetylation (DAC) is defined as the average number of D-glucosamine units per 100 monomers expressed as a percentage. It determines the content of free amino groups ($-NH_2$) in the chitosan and is one of the most important chemical characteristics that influence the physicochemical properties, biological properties,

antibacterial activity and applications of chitosan. In other words DAC value determines the functionality, reactivity, polarity and water solubility of the polymer. Chitin does not dissolve in dilute acetic acid. When chitin is deacetylated to a certain degree (~ 60% deacetylation) where it becomes soluble in the acid, it is referred to as chitosan [21, 31].

The DAC value can be obtained directly by determining amino group content of a chitosan sample or indirectly by determining acetyl content (degree of *N*-acetylation). Acid-base titration is one of the simplest methods to determine DD which involves dissolving a known amount of chitosan in an excess of dilute acid (e.g. hydrochloric acid), titrating it with a standard sodium hydroxide solution and measuring the pH to determine the stoichiometry. Conductometric titrations can be the convenient way [32]. Other methods used to determine the DD are IR spectroscopy [33], UV spectroscopy [34], ^{1}HNMR spectroscopy [35, 36], 13C solid-state NMR spectroscopy [37], gel permeation chromatography [34], elemental analysis [38] etc

1.5.3 Molecular weight

The molecular weight of chitosan is another important property that determines its suitability for a particular application. It determines the viscosity of its solution and the strength of chitosan fibre and film. The molecular weight of chitin and chitosan depend on its source and deacetylation conditions (time, temperature, and concentration of NaOH), respectively [2,3]. Molecular weight of chitosan mostly determined by Viscometry [39], gel permeation chromatography [40] and light scattering spectrophotometry [32]. Chitosan obtained from deacetylation of crustacean chitin may have a molecular weight over 10^5~10^6. Consequently, it is necessary to reduce the molecular weight by chemical methods to much lower molecular weight for easy application as a textile finish.

Depolymerisation is a process of preparation of low molecular weight chitosan from high molecular weight chitosan. It can be achieved by chemical, physical and enzymatic methods. Chemical depolymerisation using hydrochloric acid, nitrous acid and phosphoric acid have been attempted [41-43]. The enzymatic depolymerisation with chitosanase [42, 44] is milder and easy to control but is expensive. Oxidative depolymerisation using ozone [45] and hydrogen peroxide [46] has also been reported.

Physical methods such as ultrasonification [47], irradiation [48, 49] have been attempted by researchers.

1.5.4 Solubility

The solubility of chitosan is very important for its utilization, such as for chemical modification and film or fiber formation. Neither chitin nor chitosan are soluble in neutral water. Chitin is a semicrystalline polymer with extensive inter- and intramolecular hydrogen bonds, which make it difficult to dissolve in dilute acids or organic solvents under mild conditions. Although the polymer backbone consists of hydrophilic functional groups chitosan is normally insoluble in water and most common organic solvents (e.g. DMSO, DMF, NMP, organic alcohols, pyridine). The insolubility of chitosan in aqueous and organic solvents is a result of its crystalline structure, which is attributed to extensive intramolecular and intermolecular hydrogen bonding between the chains and sheets, respectively (Figure 1.5) [50, 51].

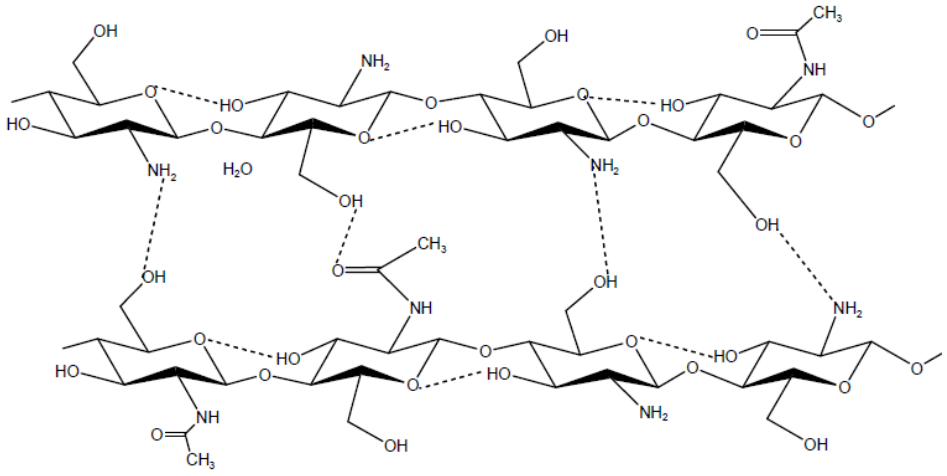


Figure 1.5 Crystalline structure of chitosan

The pKa value of chitosan is 6.3 and is therefore soluble in dilute mineral or organic acids by protonation of free amino groups at pH below about 6.5. This cationic nature is the basis of a number of applications of chitosan. Acetic and formic acids are most widely used for research and applications of chitosan [52]. The solubility of chitosan is determined by molecular weight, DAC value and pH and ionic valency of acid used. Generally, the solubility of chitin and chitosan decreases with an increase in

molecular weight. Oligomers of chitin and chitosan with a degree of polymerization (DP) of 8 or less are water-soluble regardless of pH. When chitin is deacetylated to a certain degree (~ 60% deacetylation) where it becomes soluble in the acid, it is referred to as chitosan [21]. Polyions such as pentasodium tri polyphosphate (TPP), EDTA etc lead to gel ionization at certain concentration and then precipitation at higher concentrations of acid [53-56]. Chitosan also precipitates in sulphuric acid solution [57, 58]. Such polyionic acids can be employed in the synthesis of nano- chitosan particles, which is discussed elaborately in chapter 3.

1.5.5 Viscosity

Viscosity of chitosan solution is another property that determines its commercial applications and is determined by the degree of deacetylation, molecular weight, concentration, ionic strength, pH, and temperature [59]. The viscosity of chitosan increases with an increase in molecular weight and concentration of chitosan, while it increases with decrease in pH in acetic acid and decreases with decreasing pH in HCl. Moreover, the antimicrobial activity of chitosan is also affected by its viscosity [60]. Several studies have shown that physical and chemical treatments affect its viscosity. Viscosity of chitosan decreased with increasing treatment time of grinding, heating, autoclaving, ultrasonication and ozonation [61], and decreased from 248 to 32 cP with increasing deproteinization time from 0 to 30 min [62].

In aqueous solutions, above certain polymer concentration, intermolecular interactions lead to the formation of associations thus exhibiting thickening properties. The viscous solution shows Newtonian flow. Viscosity can be used to determine the molecular weight of chitosan. Viscosity behaviour of chitosan and its different derivatives is discussed elaborately forthcoming chapters.

1.5.6 Chitosan hydrogel

Hydrogels are the crosslinked polymer networks that hold a large amount of water. The polymers used to prepare hydrogels normally consist of a large portion of hydrophilic groups and the formed networks are prevented from dissolving due to the chemical or physical bonds between the polymer chains. Water can penetrate into the

networks, resulting in the swelling of the hydrogels. Depending on the methods fabrication, the dimensions of hydrogels can vary from nanometer to centimeters in width and in different shapes such as films, capsules, sponges, microparticles, composites, beads, etc.

Chitosan based gels may be broadly divided into thermally reversible gels and non reversible gels. Reversible gels are normally obtained by physical cross linking via ionic gelation with anionic molecules while non reversible gels are produced by *N*-acylation and Schiff's base (aldemide) formation. One of the simplest ways to prepare chitosan gel is to treat chitosan acetate solution with carbodiimide. Chitosan hydrogel beads by physically crosslinked with TPP was developed as a pH-sensitive drug release system to encapsulate glipizide, an insulin stimulating drug. The hydrogel beads were proposed to release the encapsulated drug slowly uponsubcutaneous injection, with good tolerability and prolonged half life [63]. In chemical crosslinking, the Schiff's base formation system with dialdehydes such as glyoxal, glutarldehyde etc is the most widely accepted one. This involves the covalent cross linkages formation between chains [2].

Chitosan hydrogel found several applications due their unique features depending on the polymer used, including slow release profile due to physical or chemical crosslinking, enhanced drug residence time and tissue permeability, mucoadhesive characteristics, survival against gastrointestinal tract and colon delivery, etc. The chitosan–polyphosphoric acid gel bead is used as a carrier for the sustained release of anticancer drugs in simulated intestinal and gastric juice. Further, for food industry, hydrogel beads may be more feasible to achieve and industrialize, due to the low cost and controllable preparation parameters, and scalable procedures, compared with nano/microparticles delivery systems in food industry. Hydrogels are also used as a media for affinity chromatography for enzymes, media for gel permeation chromatography, for the isolation of bovine serum albumin, and a wound dressing materials [2, 3, 64-66].

1.5.7 Chitosan membranes

Chitosan, particularly high molecular weight, exhibits good film-forming properties as a result of intra- and intermolecular hydrogen bonding. The films are mostly

flexible, tough, transparent, and colourless with smooth and shiny surface. The quality of film depends on the source from which the precursor 'chitin' is obtained. The films of squid-pen chitosan are clearer and rigid than that of crab and cray fish chitosan [22]. Chitosan films, in general, are produced from acidic solutions containing volatile acid such as formic or acetic acid. The viscous solution is spread on glass plate and dried on water bath to evaporate the acid and moisture. The film i.e. chitosan formate or acetate, which is soluble in water, is detached from glass sheet and the treated with 1M NaOH solution and washed thoroughly to neutral pH and then dried at 60 ^{0}C [67].

The film of chitosan takes place through a series of phases. When the polymer solution is cast on a surface, cohesion forces form a bond between the polymer molecules. When the cohesive strength of the polymer molecules is relatively high, continuous surfaces of the polymer material coalesce. Coalescence of an adjacent polymer molecule layer occurs through diffusion. Upon evaporation of water, gelation progresses and allows the polymer chains to align in close proximity to each other and to get deposited over a previous polymer layer. When there is adequate cohesive attraction between the molecules, sufficient diffusion, and complete evaporation of water, polymer chains align themselves to form films [68].

Chitosan membranes are useful in selective isolation of heavy metals ions such as copper, cadmium, cobalt, molybdenum, zinc, mercury, chromium etc. Other applications are in edible films for coated food and tablets, tissue engineering etc. These are used as active transport membrane for halogen and organic ions in protein purification, as affinity membrane for purification lysozyme, in dialysis, in reverse osmosis and ultrafiltration [3, 5, 69].

1.5.8 Chitosan beads

Chitosan is known to chelate heavy metal ions by residual amino groups, it was expected that the chelating capacity and adsorption for heavy metal ions or organic compounds could be modified by reforming standard chitosan into other forms with increased relative surface. Chitosan formed in porous beads seems to be the most suitable shape for industrial applications in waste water treatment. Chitosan beads find several miscellaneous applications such as media for anion exchange and affinity

chromatography, as controlled release carriers for drug and agrochemicals, as encapsulating materials for mammalian cells, microbes, and drugs and for immobilization of enzymes [1, 3]. The fabrication of chitosan beads, chitosan of suitable molecular weight and desired concentration is first prepared in acidic aqueous solution. A viscosity regulator such as sodium acetate or urea may also be added to chitosan solution. The chitosan solution is poured into a coagulating bath through a discharge hole. The coagulating bath is normally alkaline containing any one of the following: sodium hydroxide, potassium hydroxide, ammonia, ethylene diamine etc preferably in presence of alcohol (e.g. methanol). Alcohol reduces the surface tension of bath and moderates the shocks during pouring and therefore control the specific surface area[70].

1.5.9 Chitosan fibres

The linear structure of chitosan is mainly responsible for the fibre forming property. Chitosan fibres are produced by wet spinning method. Chitosan is dissolved in acetic acid to give a solution of 3% w/v and then extruded through the spinneret into a caustic coagulation bath (0.5%) to obtain a regenerated fibre. Chitosan fibres find use in the production of textiles having antimicrobial, antithrombogenic, haemostatic, deodorizing, moisture controlling, and non allergenic properties which are intern used as bandages for wound- dressing, as sutures, as perfume releasing fabrics, carriers to for active drugs and artificial limbs [1, 3, 71].

1.6 BIOLOGICAL PROPERTIES OF CHITOSAN

1.6.1 Biodegradability

Chitin and chitosan are biodegradable in the biosphere, in the agriculture soil, and in the hydrosphere to produce oligosaccharides [3]. These are mostly attacked, *in vivo*, by several non specific proteases such as lysozyme, papain, pepsin etc. present in all mammalian tissues. Their biodegradation leads to the release of non toxic oligosaccharides of variable length which can be subsequently incorporated to glycosaminoglycans and glycoproteins, to metabolic pathways or be excreted. The rate of degradation is governed by molecular weight, degree of deacetylation (DAC) and the distribution of acetyl groups. The absence of acetyl groups or their homogeneous

distribution (random rather than block) are reported in very low rates of enzymatic degradation. This occurs due to differences in deacetylation conditions which influences viscosity of the chitosan solution by changing the inter- or intra-molecular repulsion forces. The degradation rate influnces the biocompatibility since very fast rates of degradation will produce an accumulation of the amino sugars and produce an inflammatory response. Chitosan samples with low DAC induce an acute inflammatory response while chitosan samples with high DAC induce a minimal response due to the low degradation rate. Degradation has been shown to increase as DAC decreases [10, 72, 73].

1.6.2 Non toxicity and biocompatibility

Chitosan is totally non toxic and its degradation products namely glucosamines are biocompatible. Although the gastrointestinal enzymes can partially degrade both chitin and chitosan, when both polymers are orally administered they are not absorbed. For this reason, they are considered as not bioavailable. Chitosan shows a LD_{50} of around 16g/kg, very similar to the salt and glucose values in assays carried out on mice. LD_{50} is the amount of a material, given all at once, which causes the death of 50% (one half) of a group of test animals. No abnormal symptoms are observed with several animals after the oral administration of chitosan for 8 months at a daily dose of 0.7-0.8 g per kg body weight, and after the intravenous injection of low molecular weight chitosan for 11 days at a daily dose of 4.5 mg per kg body weight [3, 74].

Toxicity of chitosan is reported to depend on DAC, which decreases with increase in DAC. On the other hand, Mw of chitosan did not influence toxicity [74]. Chitosan presents higher cytocompatibility *in vitro* than chitin. The cytocompatibility of chitosan has been proved *in vitro* with myocardial, endothelial and epithellial cells, fibroblast, hepatocytes, condrocytes and keratinocytes [75]. This property seems to be related to the DD of the samples. When the positive charge of the polymer increases, the interactions between chitosan and the cells increase too, due to the presence of free amino groups [10].

1.6.3 Antimicrobial activity

One of the most unique biological properties of chitosan is its antibacterial activity against different groups of microorganisms, such as bacteria, yeast, and fungi. This unique property, due to the polycationic nature of chitosan, facilitated its application in a variety of fields, including food science, agriculture, medicine, pharmaceutics, and textiles. Different mechanisms are proposed to explain the inhibition of microbial cells by chitosan. A positive charge on the amine group of the glucosamine monomer at pH<6.3 allows interactions with negatively charged microbial cell membranes that lead to the leakage of intracellular constituents. Also, the interaction with anionic groups on the cell surface causes the formation of an impermeable layer around the cell, which prevents the transport of essential solutes [76]. The second mechanism involves the inhibition of the RNA and protein synthesis by permeation into the cell nucleus [77]. Other mechanisms have also been proposed. Chitosan may inhibit microbial growth by acting as a chelating agent rendering metals, trace elements or essential nutrients unavailable for the organism to grow at the normal rate [78]. It has also been proposed that the antimicrobial action of chitosan against filamentous fungi could be explained by a more direct disturbance of membrane function [79]. Thus, any modifications that increase the cationic charge on the polymer surface, increase the fluidity and impart the chelation property are key factors determining the antimicrobial efficiency of chitosan. Cationic charge is increased by lowering the pH, increased DAC and increased degree of quaternization. Permeability is associated with molecular weight/viscosity and the particle size (hydrodynamic volume) of chitosan, which should be lower [10, 77, 80]. The antibacterial property of chitosan is also variable on the type of the bacteria [7, 81]. Chitosan has shown stronger bactericidal effect on gram-positive bacteria (*Listeria monocytogenes, Bacillus megaterium, B. cereus, Staphylococcus aureus, Lactobacillus plantarum, L. brevis, and L. bulgaris*) than on gramnegative bacteria (*E.coli, Pseudomonas fluorescens, Salmonella typhymurium, and Vibrio parahaemolyticus*).

Besides above properties, chitosan exhibits several other biological properties which are of interest to medical and other relevant areas, such as: antiviral, antacid, haemostatic, analgesic, antitumor, mucoadhesive, fat binding, permeation enhancer, anticholesterolemic, antioxidant, wound healing, sequestering etc [10, 82, 83].

1.7 CHEMICAL PROPERTIES OF CHITOSAN

Chitosan possesses three reactive groups, viz., primary (C-6) and secondary (C-3) hydroxyl groups on each repeat unit, and the amino group at the C-2 position on each deacetylated unit. These reactive groups can be chemically modified to alter the mechanical and physical properties, and solubility of chitosan. The typical reactions involving the hydroxyl groups of chitosan are etherification and esterification. The nucleophilic amino group in chitosan allows reactions such as *N*-alkylation, *N*-acylation and reductive alkylation by reacting chitosan with alkyl halides, acid chlorides and aldehydes or ketones, respectively. Selective *O*-substitution can be carried out by protecting the amino group during the reaction. Cross-linking or graft copolymerization can also be carried out to modify chitosan [3, 82, 83].

1.8 APPLICATIONS OF CHITOSAN

Chitosan is versatile biopolymer derived from chitin with abundance ranking next to cellulose and is renewable. The major driving force in the development of new applications for chitosan lies in the fact that the polymer is biodegradable, biocompatible, and possesses selective adsorption properties. Attributing to the polycationic nature and several inherent properties, chitosan is currently receiving a great deal of interest as regards to its applications in several diversified areas such as medical, food, textiles, water processing, cosmetics, agriculture, paper etc. An overview on applications of chitosan and its derivatives is presented below.

1.8.1 Agriculture

Chitosan has many potential applications in agriculture for its essentially biodegradable characteristics. It is used primarily as a plant growth enhancer, and as an ecofriendly biopesticide substance that boosts the ability of plants to defend against fungal infections such as *Fusarium solani*. Chitosan triggers the defensive mechanisms in plants, acting much like a vaccine in humans. The biocontrol mode of action of chitosan elicits natural innate defense responses within plant to resist insects, pathogens, and soil-borne diseases when applied to foliage or the soil [84, 85].

In addition to growth stimulation properties, chitosan is used for seed-coating on cotton, corn, seed potatoes, soybeans, sugar beets, tomatoes, wheat etc, frost protection, protective coating for fruits and vegetables, controlled release of fertilizers, nutrients etc into the soil**.** Chitosan increases photosynthesis, promotes and enhances plant growth, stimulates nutrient uptake, increases germination and sprouting, and boosts plant vigor. [5, 86].

1.8.2 Applications in food technology

Chitosan has been already been used as a food ingredient in Japan, Europe and in United States as a lipid trap, an important dietetic breakthrough. Since, chitosan is not digested by the human body; it acts as a fibre, a crucial diet component. It binds the lipids arriving in the intestine, thereby reducing the cholesterol absorption by about 20 to 30% by the human body [10, 87].

Chitosan and its derivatives has a significant role in food application area in view of recent outbreaks of contaminations associated with food products as well as growing concerns regarding the negative environmental impact of packaging materials currently in use. Chitosan can be used in meat preservation by inhibiting some meat spoilage bacteria such as *Pseudomonas fragi, Bacillus subtilis, Escherichia coli,* and *Staphylococcus aureus* and some meat starter cultures namely *Lactobacillus plantarium, Pediococcus pentosaceus,* and *Micrococcus varians*. The addition of sunflower oil to chitosan-based films improves gloss of films and the water vapour barrier properties when acetic acid was used as a solvent to prepare the films. Besides, chitosan films can be used as a packaging material for the quality preservation of a variety of food [10, 88, 89].

1.8.3 Applications of chitosan in cosmetics

A cosmetic is defined as any substance to be placed in contact with various surface parts of the human body (e.g. epidermis, hair systems, nails, lips, and external genital organs), or with teeth and the mucous membranes of the oral cavity with a view exclusively or principally to perfume them, protect them, and keep them in good condition, to change their appearance, or to correct body odour. Chitosan is a natural

cationic gum that has been used for various cosmetic applications, it is used to maintain skin moisture, treat acne, tone skin, protect epidermis, reduce static electricity in hair, fight dandruff etc. Incorporation of chitosan salt in shampoos confer shine and strength to hair due to the ionic interactions between chitosan and hair proteins. When applied to the surface of the skin, chitosan forms a protective and moisturizing elastic film[5, 90].

1.8.4 Applications of chitosan in biomedicine

It is in the field of health that the many properties of chitosan (bacteriostatic, immunologic, antitumoral, cicatrizant, hemostatic and anticoagulant) are of interest. For example, because of its biocompatibility with human tissue, chitosan's cicatrizant properties have proven its effectiveness as a component, notably, in all types of dressings (artificial skin, corneal dressings, etc.), surgical sutures, dental implants, in rebuilding bones and gums, and in opthalmological applications. Due to the high *N*-amino content, chitosan acts as a powerful natural magnetic attraction for lipids, fats, and bile in the digestive tract, and actually binds with them to prevent their absorption into the bloodstream. The attracting ability of chitosan can possibly reduce cholesterol and triglycerides blood plasma levels, which contribute to obesity and cardiovascular disease. Various hypolipemic formulations including particles, powders, solutions, and injections containing chitosan, were prepared for oral administration [5, 10, 82,91,92].

It is known that compounds having molecular weights less than 2900 pass through membranes derived from chitosan. Attributing to non hazardous nature and inexpensive, chitosan may be suitable for use in the preparation of dosage form commercial drugs. With reference to pharmaceutical excipient for directly compressed tablets, chitosan-alginate combination showed an extended drug release property. Dry coated tablets having a long induction period in drug release have been prepared by an ion-complex of alginate-chitosan. Sustained intestinal delivery of drugs such as 5-fluorouracil (choice drug for colon carcinomas) and insulin (for diabetes mellitus) seems to be a feasible alternative to injection therapy. For the latter, the drug should be delivered at proper sites (intestine) for long duration for producing maximum pharmacological activity. Sustained release of oxytetracycline, an antibiotic agent, from chitosan microspheres (5-30 μ) for

both oral administration and injection has been reported**.** This can be prepared by spray hardening and interfacial acylation methods [10, 82, 83, 93].

Tissue engineering is the development is the development and manipulation of laboratory grown cells, tissues or organs that would replace or support the function of defective or injured parts of the body. Chitosan is a promising polymer as a supporting material for tissue engineering for its non-toxicity, biocompatibility, biodegradability, porous structure, gel forming properties, ease of chemical modification, high affinity to in vivo macromolecules, and so on. [5, 82, 108, 94].

1.8.5 Paper industry

Biodegradable chitin and chitosan can strengthen recycled paper and increase the environmental friendliness of packaging and other product. Chitosan is already involved in the manufacture of paper because chitosan molecules greatly resemble those of cellulose the fain constituent of plant walls [5, 82]. Chitosan can be a useful component in paper printing due its film forming property. Coating of paper with chitosan/gelatine coatings improves dye fixation on the paper and kept the light fastness of the printed image. In ink jet printing, pigment based ink jet inks containing a polystyrene maleic anhydride polymer system that reacts with a fixer fluid containing chitosan salt such as chitosan acetate. A gel precipitate is formed on the substrate by the interaction of the chitosan in the fixer fluid and the reactive polymer system in the ink. The gel forms a protective film on the substrate providing benefits such as increased drying time, smear fastness, smudge fastness and water fastness [95].

1.8.6 Chromatography

Chitosans find wide variety of applications in chromatographic separations. The presence of free amino and hydroxyl groups in chitosan makes it an useful chromatographic support. Chitosan can be used in thin layer chromatography for separation of nucleic acid and solid phase extraction of phenols and chlorophenols [82].

1.8.7 Solid state batteries

Chitosan dissolved acetic acid solution can be employed for the fabrication of solid state proton conducting batteries. The conductivity is due to the transport of protons through microvoids in polymer. Small dielectric constants from piezoelectric studies attributed the presence of many microvoids in polymer structure. The choice of a more stable electrode material may produce better battery system [82].

1.8.8 Biocatalysis

Chitosan is widely used as supports for enzyme and cell immobilization due to its appropriate characteristics. Immobilization is the process in which the enzyme, cells or organelles is confined in a definite position thus rendering an insoluble form which retains the catalytic activity and can be reused several times[10, 83].

1.8.9 Molecularly imprinted materials

Chitosan, due to the presence of reactive sites, can be used in making molecularly imprinted polymeric matrices. Molecularly imprinted polymer represents a new class of materials that have artificially created receptor structures. This potential technology is a method for making selective binding sites in polymers by using a molecular template. These have steric and chemical memory toward the template and hence could be used to rebind it. Choice template for bio fabrication is mainly rendered on the end use such as dibenzothiophene sulfone for fuel desulfurization, hemoglobin for protein binding, nikel or copper for metal recovery and photodegradation etc [10].

1.8.10 Water processing

Chitosan can also be used in water processing engineering as a part of a filtration process. Chitosan causes the fine sediment particles to bind together and is subsequently removed with the sediment during sand filtration. Chitosan also removes phosphorus, heavy minerals, and oils from the water. Chitosan is an important additive in the filtration process. Sand filtration apparently can remove up to 50% of the turbidity alone while the chitosan with sand filtration removes up to 99% turbidity [5, 82, 96, 97]. Chapter 5 covers various aspects regarding applications chitosan in context to water processing.

1.8.11 Textiles

In textiles, it finds applications in the primary production of fibers (useful for sutures, wound dressings etc), in the manufacture of textile auxiliary chemicals and finishing agents. Investigations have shown that it can be used as a dye fixing agent, for shade and neps coverage, to improve the fastness of dyed fabrics, as a binder in pigment printing, as a thickener in printing. Due to its unique ability to dissolve and bind fats, it can be used as soil repellant agent. By virtue of its bacteria impeding property, chitosan can prevent garments to develop bad odour. Detailed studies on the applications chitosan and its derivetives in textiles are discussed in subsequent chapters.

REFERENCES

1. Henryk Struszczyk, Olli Kivekas, Antoni Niekraszewicz and Alojzy Urbanonowski, "Chitosan-new forms and uses", *Textile Asia*, July (1993) 80-83
2. M. Terbojevich and R.A.A. Muzzarelli, "Chitosan" *Handbook of Hydrocolloids*, G.O.Phillips and P.A. Williams (Eds), Woodhead Publishing Ltd, Cambridge, England (2000) 367- 378
3. S. Hirano, 'Chitin and Chitosan', *Ullmann's Encyclopedia of Industrial Chemistry*, Wiely-VCH, **6** (2003) 679-691
4. http://dalwoo.com/chitosan/applications.html
5. Gavhane Yogeshkumar N., Gurav Atul S. and Yadav Adhikrao V., "Chitosan and Its Applications: A Review of Literature", *International Journal of Research in Pharmaceutical and Biomedical Sciences*, **4** (1) (2013) 312-331
6. L.L. Davis and S. Bartnicki-Garcia, "Chitosan synthesis by the tandem action of chitin synthetase and chitin deacetylase from Mucor rouxii ", *Biochemistry*, **23(6)** (1984) 1065-73
7. H.K. No, N.Y. Park, S.H. Lee and S.P. Meyers, " Antibacterial activity of chitosans and chitosan oligomers with different molecular weights", *International Journal of Food Microbiology*, **74** (2002) 65-72
8. D.H. Davies, C.M. Elson and E.R.N. Hayes, "O-carboxy methylchitosan, a new water soluble chitin derivative", *Chitin and Chitosan*, G. Skjakbreak, T. Anthonsen, and P. Sanford (Eds), Elseiver Applied Science, London, (1989)

467-472

9. S. Hirano, "Application of chitin and chitosan in the ecological and environmental fields", *Application of Chitin and Chitosan*, M.F.A. Goosen (Ed.), Technomic Publishing Corporation, Inc, Lancaster, PA (1997) 31-54
10. A. Inmaculada, M.Marian, H.Ruth, P. Inés, M. Beatriz, A. Niuris, G. Gemma and H. Ángeles, "Functional Characterization of Chitin and Chitosan", *Current Chemical Biology*, **3** (2009) 203-230
11. B.S. Bahl and Arun Tuli, Advanced Organic Chemistry, 2nd edition, S. Chand and Co Ltd., N. Delhi (1983)
12. K.Ogawa, "Effect of heating an aqueous suspension of chitosan on the crystallinity and polymorphs", *Agricutural and Biological Chemistry*, **55**(1991) 2375– 2379
13. Y. Inoue, "NMR determination of degree of acetylation" in: *Chitin Handbook* , R.A.A. Muzzarelli, and M.G. Peter, (Eds), Atec, Grottammare, Itali (1997) 133-136
14. M.G. Peter, R.A.A. Muzzarelli and A Domard (Eds), *Advances in Chitin Science*, Univ. Potsdam, **4** (2000)
15. G.A.F. Roberts, *Chtin Chemistry*", Macmillam Press, London (1992)
16. Mukesh Kumar Singh, "21st century with deodorant fabrics", *Man Made Textiles In India*, **14** (7) (2002) 279-286
17. Vivek L. Singh, "Biopolymers", *Asian Textile Journal*, (1-2) (2005) 65-68
18. N. Sekar, "Chitosan in textile processing-an update", *Colourage*, **XLVII** (7) (2000) 33-34
19. Kh.F.El.Tahlawy, "Utilization of citric acid – chitosan, sodium hypophosphite system for effecting concurrent dyeing and finishing", *Colourage*, **XLVI** (5) (1999) 21-26
20. M.W. Anthonsen, K.M. Varum, and O. Smidsrod, "Solution properties of chitosans: conformation and chain stiffness of chitosans with different degrees of *N*-acetylation", *Carbohydrate Research*, **256** (1) (1994)159–75
21. H.K. No, and S.P. Meyers, "Preparation and characterization of chitin and chitosan- A Review", *Journal of Aquatic Food Product Technology*, **49** (2)

(1995) 27-52

22. R. Shephard, S. Reader and A. Falshaw, "Chitosan Functional Properties", *Glycoconjugate Journal,* **14** (1997) 535-42
23. D.R. Kreger, "Observations on cell walls of yeast and some other fungi by X-ray diffraction and solubility tests ", *Biochimica et Biophysica Acta,* **13** (1954) 1-9
24. K.Tokuyasu, M.Ohnishi-Kameyama, K.Hayashi, "Purification and characterization of extracellular chitin deacetylase from Colletotrichum lindemuthianum", *Bioscience, Biotechnology and Biochemistry*, **60** (1996) 1598-1603
25. A. Martinou, U. Bowitis, B.Stokke and K.M.varumd, *Carbohydrate Research,* **311**(1-2) (1998)17-24
26. R.H. Hackman and M. Goldberg, "Studies on chitin. VI. The nature of alpha- and beta-chitins", *Australian Journal of Biological Sciences,* **18**(4) (1965) 935-946
27. T. Sannan, K. Kurita and Y. Iwakura, "Studies on chitin, 1. Solubility change by alkaline treatment and film casting", *Makromolekular Chemistry and Physics,* **176**(4) (1975) 1191-1195
28. S. P. Meyers, H. K. No and K. S. Lee, "Isolation and characterization of chitin from crawfish shell waste", *Journal of Agricultural and Food Chemistry,* **37** (3) (1989) 575-579
29. F. Shahidi and J. Synowiecki, "Isolation and charactrization of nutrients and value added products from snow crab (Chinoecetes opilio) and shrimp (Pandalus borealis) processing discards", *Journal of Agricultural and Food Chemistry,* **39** (1991) 1527-1532
30. H. M. Chen and S. P. Meyers, Effect of antioxidants on stability of astaxanthin pigment in crawfish waste and oil extract, *Journal of Agricultural and Food Chemistry,* **30** (1982) 469-473
31. Y. W. Cho, J. H. Jang, C. R. Park and S. W. Ko, "Preparation and solubility in acid and water of partially deacetylated chitins", *Biomacromolecules,* **1** (2000) 609-614
32. A. Domard and M. Rinaudo, "Preparation and characterization of fully

deacetylated chitosan", *International Journal of Biological Macromolecules*, **5**(1) (1983) 49-52

33. A. Baxter, M. Dillon, K. D. A. Taylor, and G. A. F. Roberts, "Improved method for i.r. determination of the degree of *N* acetylation of chitosan", *International Journal of Biological Macromolecules*, **14** (1992) 166-169
34. S. Aiba, "Studies on chitosan: 1. Determination of the degree of *N* acetylation of chitosan by ultraviolet spectrophotometry and gel permeation chromatography", *International Journal of Biological Macromolecules*, **8** (1986) 173-176
35. Elisabete Curtia and Sergio Paulo Campana-Filho, "Viscosity Behavior of Chitosan and *N,N,N*-Trimethylchitosan Chloride Salts in Acid-Free Aqueous Solution", *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, **43** (2006) 555–572
36. Elena Bobu, Raluca Nicu, M. Lupei, Fl. Ciolacu And J. Desbrières, "Synthesis And Characterization Of *N*-Alkyl Chitosan For Papermaking Applications", *Cellulose Chem. Technol*., **45** (9-10) (2011) 619-625
37. L. Raymond, F. G. Morin, R. H. Marchessault, "Degree of deacetylation of chitosan using conductometric titration and solid-state NMR", *Carbohydrate Research*, **246** (1993) 331-336
38. Wei Liang XU, Jun WU, Chun Ling FU, "Synthesis of Chitosan Quaternary Ammonium Salts", *Chinese Chemical Letters*, **12** (12) (2001)1081-1084
39. Jonathan Z. Knaul, Mohammad R. Kassai, V.Tam Bui and Katherine A M Greber, "Characterization of deacetylated chitosan and chitosan molecular weight –review", *Canadian Journal of Chemistry*, **76**(11) (1998) 1699- 1706
40. M. H. Ottoy, K. M. Varum, B. E. Christensen, M. W. Anthonsen, and O. Smidsrod, "Preparative and analytical size-exclusion chromatography of chitosans", *Carbohydrate Polymers.*, **31**(4) (1996) 253-261
41. A. Hebeish, A.Waly and A. Aou-Okeil, "The effect of molecular weight of chitosan on cotton fabric treated with citric acid and its impact on dyeing with some acid dyes", *Journal of the Textile Association*, **65** (5), Jan-Feb (2005) 219-227
42. D. Knittel, G. Materne and E. Schollmeyer, "Degradation of chitosan sizes",

Melliand English, **87**(9) (2006) E 142-E144

43. Ha-Soo Seaong, Jae-Pil Kim and Sohk- Won Ko, "Preparing chito-oligosaccharide as antimicrobial agents for cotton", *Textile Research Journal*, **69** (7) July (1999) 483-488
44. F. Lee, W.K. Lee, M.Y. Maskat, R.M. Illias, S.A. Aziz, K. Kamarulzaman and H. Osman, "Partial depolymerization of chitosan with the aid of bromelain", *Pakistan Journal of Biological Sciences*, **8**(01) (2005) 73-77
45. N. N. Kabal'nova, K. Y. Murinov, R. Mullagaliev, N. N. Krasnogorskaya, V. V. Shereshovets, Y. B. Monakov and G. E. Zaikov, "Oxidative destruction of chitosan under effect of ozone and hydrogen peroxide", *Journal of Applied Polymer Science.*, **81** (2001) 875-881
46. Feng Tian , Yu Liu, Keao Hu, Binyuan Zhao, "The depolymerization mechanism of chitosan by hydrogen peroxide" *Journal of Materials Science*, **38** (2003) 4709 – 4712
47. S. Baxter, S. Zivanovic and J. Weiss, "Molecular weight and degree of acetylation of high-intensity ultrasonicated chitosan", *Food Hydrocolloids*, **19** (2005) 821-830
48. S. Trzciński, "Combined Degradation of Chitosans", *Polish Chitin Society*, Monograph XI (2006) 103-111
49. W.S. Choi, K.J. Ahn, D.W. Lee, M.W. Byun and H.J. Park, "Preparation of chitosan oligomers by irradiation", *Polymer Degradation and Stability*, **78**, (2002) 533-538
50. T. Yui, K. Imada, K. Okuyama, Y. Obata, K. Suzuki and K. Ogawa, "Molecular and crystal structure of the anhydrous form of chitosan", *Macromolecules*, **27**(26) (1994) 7601-7605
51. K. Kurita, M. Kamiya and S. Nishimura, "Solubilization of a rigid polysaccharide: controlled partial *N*-acetylation of chitosan to develop solubility", *Carbohydrate Polymers*, **16**(1991) 83-92
52. T. Rathke and S. Hudson, "Review of chitin and chitosan as fiber and film formers", *Journal of Macromolecular Science R. M. C.*, **C34**(3) (1994) 375-437
53. T. Lopez-Leon, E.L.S.Carvalho, B.Seijo, J.L.Ortega-Vinuesa, D. Bastos-

Gonzalez, "Physicochemical characterization of chitosan nanoparticles: electrokinetic and stability behavior", *Journal of Colloid and Interface Science*, **283**, (2005) 344–351

54. Hong-liang Zhang, Si-hui Wu, Yi Tao, Lin-quan Zang, and Zheng-quan Su, "Preparation and Characterization of Water-Soluble Chitosan Nanoparticles as Protein Delivery System", *Journal of Nanomaterials*, **2010** (2010), 1-5
55. Huacai Ge and Shiying Huang, "Microwave Preparation and Adsorption Properties of EDTA-Modified Cross-Linked Chitosan", *Journal of Applied Polymer Science*, **115** (2010) 514–519
56. B. Loretz, and A. Bernkop–Schnürch, "In vitro evaluation of chitosan–EDTA conjugate polyplexes as a nanoparticulate gene delivery system", *AAPS Journal*, **8**(4) (2006) art. no. 85
57. Mayyas M.A. Al-Remawi, "Properties of chitosan nanoparticles formed using sulfate anions as crosslinking bridges", *American Journal of Applied Sciences*, **9** (7) (2012) 1091-1100
58. Xiao Ling, Yu Zu-yu, Yang Chao, Zhu Hua-yue and Du Yu-min, "Swelling studies of chitosan-gelatin films cross-linked by sulfate", *Wuhan University Journal of Natural Sciences*, **9**(2) (2004) 247-251
59. Q. Li, E.T. Dunn, E.W. Grandmaison and M.F.Goosen, "Applications and properties of chitosan*", Journal of Bioactive and Compatible Polymers*, **7**(1992) 370-397
60. Y.I. Cho, H.K. No and S.P. Meyers, "Physicochemical characteristics and functional properties of various commercial chitin and chitosan products", *Journal of Agricultural and Food Chemistry*, **46** (1998) 3839-3843
61. H.K. No, S.D. Kim, D.S. Kim, S.K. Kim and S.P. Meyers, "Effect of physical and chemical treatment on chitosan viscosity", *Journal of Chitin and Chitosan*, **4**(4) (1999) 177-183
62. H.K. No, S.H. Lee, N.Y. Park and S.P. Meyers, "Comparison of physicochemical, binding, and antibacterial properties of chitosans prepared without and with deproteinization process", *Journal of Agricultural and Food Chemistry*, **51**(2003) 7659-7663

63. P. Sun, P. Li, Y. M. Li, Q. Wei and L. H. Tian, "A pH-sensitive chitosan-tripolyphosphate hydrogel beads for controlled glipizide delivery", *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, **97**(1) (2011) 175-183

64. B. Krajewska, "Application of chitin-and chitosan-based materials for enzyme immobilizations: a review", *Enzyme and Microbial Technology*, **35**(2) (2004) 126-139

65. A. Elzatahry, M. Eldin, E. Soliman and E. Hassan, "Evaluation of alginate–chitosan bioadhesive beads as a drug delivery system for the controlled release of theophylline", *Journal of Applied Polymer Science*, **111**(5) (2009) 2452-2459

66. J. Yang, J. Chen, D. Pan, Y. Wan and Z. Wang, "pH-sensitive interpenetrating network hydrogels based on chitosan derivatives and alginate for oral drug delivery", *Carbohydrate Polymers*, **92** (01)(2013) 719-725

67. J. L. Wiles, P.J. Vergano, F.H. Barron, J.M. Bunn and R.F. Testin, "Water vapor transmission rates and sorption behaviour of chitosan films", *Journal of Food Science*, **65**(7) (2000) 1175-1179

68. G.S. Banker, "Film coating theory and practice", *Journal of Pharmaceutical Sciences*, **55 (1)** (1966) 81-89

69. W. Kamiñski and Z. Modrzejewska, "Application of chitosan membranes in separation of heavy metal ions", *Seperation Science and Technology*, **32** (16) (1997) 2659 – 2668

70. G.L. Rorrer, T.Y. Hsien and J.D. Way, "Synthesis of porous-magnetic chitosan beads for removal of cadmium ions from waste water", *Industrial Engineering and Chemical Research*, **32** (1993) 2170–2178

71. S. Sudha, V.R. Giridev, R. Neelkandan and M.S. Kumar, "Chitosan. – A versatile polymer for textile applications." *Journal of the Textile Association*, **64** (4) (2006) 165-166

72. H. Sashiwa, H. Saimoto, Y. Shigemasa, R. Ogawa and S. Tokura, "Distribution of the acetamide group in partially deacetylated chitins", *Carbohydrate Polymers*, **16** (3) (1991) 291-296

73. S. Hirano, H.Tsuchida and N. Nagao, "*N*-acetylation in chitosan and the rate of

its enzymic hydrolysis", *Biomaterials*, **10**(8) (1989) 574-576

74. N.G.M. Schipper, K.Varum, P. Artursson, "Chitosans as absorption enhancers for poorly absorbable drugs. 1: influence of molecular weight and degree of acetylation on drug transport across human intestinal epithelial (Caco-2) cells", *Pharmaceutical Research*, **13**(11) (1996) 1686-1692
75. C. Chatelet, O. Damour and A. Domard, "Influence of the degree of acetylation on some biological properties of chitosan films", *Biomaterials*, **22**(3) (2001) 261-268
76. I.M. Helander, E.L. Nurmiaho-Lassila, R. Ahvenainen, J. Rhoades and S. Roller, "Chitosan disrupts the barrier properties of the outer membrane of Gram-negative bacteria", *International Journal of Food Microbiology*, **71** (2001) 235-244
77. X. F. Liu, Y. L. Guan, D. Z. Yang, Z. Li, and K. D. Yao, "Antibacterial action of chitosan and carboxymethylated chitosan", *Journal of Applied Polymer Science*, **79**(7) (2001) 1324-1335
78. S. Roller and N. Covill, "The antifungal properties of chitosan in laboratory media and apple juice", *International Journal of Food Microbiology* , **47**(1-2) (1999) 67-77
79. S.W. Fang, C.F. Li and D.Y.C. Shih, "Antifungal activity of chitosan and its preservative effect on low-sugar candied kumquat", *Journal of Food Protection*, **57** (1994) 136-40
80. G. J. Tsai and W. H. Su, "Antibacterial activity of shrimp chitosan against *Escherichia coli*", *Journal of Food Protection*, **62**(3) (1999) 239-243
81. L.Y. Zheng and J.F. Zhu, "Study on antimicrobial activity of chitosan with different molecular weights", *Carbohydrate Polymers*, **54** (2003) 527-530
82. P.K.Dutta, J.Dutta and V.S.Tripati, "Chitin and Chitosan: Chemistry, properties and applications", *Journal of Scientific and Industrial Research*, **63** (2004) 20-31
83. K.V. Harish Prashant and R.N. Tharanathan, "Chitin/Chitosan: modifications and their unlimited application potential- an overview", *Trends in food Science & Technology*. **18** (2007) 117-131

84. L. A. Hadwiger and J. M. Beckman, "Chitosan as a Component of Pea-*Fusarium solani* Interactions", *Plant Physiology*, **66**(2) (1980) 205-211

85. M. Naeem, A. Hassan , M .Ahmed and A. El- Sayed, "Radiation induced degradation of chitosan for possible use as a growth promoter in agricultural purposes", *Carbohydrate Polymers*, **79** (2010) 555–562

86. http://www.epa.gov/pesticides/biopesticides

87. S. Fereidoon, J.K.V. Arachchi and Y.J. Jeon, "Food applications of chitin and chitosans", *Trends in Food Science & Technology*, **10** (1999) 37-51

88. S. Fujii, H. Kumagai and M. Noda, "Preparation of poly(acyl)chitosans", *Carbohydrate Research*, **83(2)** (1980) 389-393

89. P.K. Dutta, S. Tripathi, G.K. Mehrotra, J. Dutta, "Perspectives for chitosan based antimicrobial films in food application", *Food Chemistry*, **114** (2009) 1173–1182

90. C.Beaulieu, "Chitin and Chitosan", http://www.plasticstrends.net/index.php?option=com_content&task=view&id=12 &Itemid=28

91. Genzyme Corporation, "Seprafilm: Adhesion Barrier, 2006", http://www.seprafilm.com/medprof/efficacy.asp

92. H. Jing, W. Su, S. Caracci, T.G. Bunning, T. Cooper and W. Adams, "Optical waveguiding and morphology of chitosan thin films", *Journal of Applied Polymer Science*, **61** (1996)1163

93. P.K. Dutta, P. Vishwanathan, L. Mimrot, and M.N.V. Ravikumar, "Use of chitosan- amine-oxide gel as drug carrier", *Journal of Polymeric Materials*, **14** (1997) 531

94. T.K. Giri, T. Amrita, A. Amit, Ajazuddin, B. Hemant and D. K. Tripathi, "Modified chitosan hydrogels as drug delivery and tissue engineering systems: present status and applications", *Acta Pharmaceutica Sinica B*, **2** (2012) 439–449

95. C. Peniche, W. A. Monal, H. Peniche and N. Acosta, "Chitosan: an attractive biocompatible polymer for microencapsulation", *Macromolecular Bioscience*, **3**(10) (2003) 511-520

96. Alan Woodmansey (March 19 2002), "Chitosan treatment of sediment laden water-Washington State I-90 Issaquah Project", *Federal Highway Administration*. U.S. Department of Transportation. Retrieved on 2006-07-10. http://www.ftwa.dot.gov/engineering/geotech

97. H. K. No, W. Prinyawiwatkul, and S. P. Meyers, "Ch 19, Treatment of Wastewaters with the Biopolymer Chitosan", in *Handbook of Carbohydrate Engineering*, Taylor & Francis Group, LLC (2005) 535-562

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF VARYING MOLECULAR WEIGHT CHITOSANS AND THEIR APPLICATION ON COTTON FABRIC

2.1 INTRODUCTION

Chitosan is polycationic biopolymer that exhibits several valuable inherent properties such as antibacterial, antifungal, antiviral, antacid, non toxic, total biodegradable as well as film formation, fiber formation, hydrogel formation etc properties. These unique properties of chitosan make it suitable for a number of textile applications. The application of chitosan in textiles can be categorized into two main domains namely in the production of fibres and in textile wet processing that includes dyeing and finishing.

The linear structure of chitosan is mainly responsible for the fibre forming property. Chitosan fibres are produced by wet spinning method. In earlier approach (1980), Chitosan was dissolved in acetic acid to give a solution of 3% w/v and then extruded through the spinneret into a caustic coagulation bath (0.5%) to obtain a regenerated fibre. The fibre strength, however, was very poor (2.2 g/d). To obtain the good fibre out of chitosan a homogeneous solution with maximum polymer to solvent ratio is required apart from non gelling tendency. Several attempts by making suitable modifications in spin dope composition and coagulation bath are reviewed in literature [1]. Spin dope composition can be modified by using urea along with acetic acid or formic acid. Extrusion of chitosan dope into a coagulating bath containing sodium acetate, sodium hydroxide, sodium dodecyl sulphate or methanol in aqueous medium was found to improve the fibre strength by reaching the tenacity to 3.8 g/d.

Chitosan fibres find use in the production of textiles having antimicrobial, antithrombogenic, haemostatic, deodorizing, moisture controlling, and non allergenic properties which are inturn used as bandages for wound- dressing, as sutures, as perfume releasing fabrics, carriers for active drugs and artificial limbs [1-3]. Haemostatic activity

---

Contents of this chapter is published in:
1) *International Journal of Polymer Science*, Vol 2010, (2010) 1-7
2) *Asian Dyer*, Vol 6, No 5, Oct (2009) 43-53

of chitosan is high when used as a high molecular weight solid. Therefore, this has been explored as a modulator of wound healing. It has been found that chitosan has the ability to form coagulum on contact with erythrocytes, defibrinated blood and washed red blood cells and therefore the bandages for wound dressing were found to be effective in regenerating skin tissue of wound area. Recently, chitosan has been proposed to serve as a non protein matrix for three dimensional tissue growths. Chitosan provides the biological primer for cell tissue proliferation. The glucosaminoglycan constitutes the wound tissue play an important role in giving structure and strength to newly formed collagen in the granulating tissue of the healing wound. Chitosan provides amino sugars which in turn can be made available to the fibroblasts that proliferate under the action of interleukin-1 for incorporation into hyaluronate and glycoaminoglycans, thus guiding ordered deposition of collagen leading to wound healing [4-6].Introduction of carboxymethyl groups on to chitosan fibres imparts typical gelling property that can absorb large quantity of fluid. These fibres were found to be more effective than the normal chitosan fibres as a wound dressing material. By holding water inside the fibre structure, such wound dressings can limit the lateral spreading of wound exudates, reduce wound maceration, and generally improve the quality of healing process [7]. Chitosan fibres can be converted back to chitin fibres by acetylation reaction with acetic anhydride. These fibres find application as surgical suture, which has enough strength for clinical uses. The suture is digestible in the tissues by lysozyme and chitinase [2]. A composite material of chitin/chitosan and cellulose are produced by mixing powder chitin/chitosan with viscose pulp and then wet spun, known as crabyon (Omikenshi). These fibers have high moisture keeping property than cellulosic fibres and have dyeability towards direct and reactive dyes. These fibres are used as textile materials for under wears, socks, etc as these keep skin from drying. At the same time, these give velvet touch and no irritation to skin .Therefore; clothes made up of these fibres are excellent for babies and old aged people, who have weak and sensitive skin [8]. Similar type of fibre exhibiting deodorant property was produced by a Kokai Tokkyo Koh (Japan), which is useful for clothing, beddings, interior materials, medical care materials, curtains and carpets [9].

Applications of chitosan in textile processing domain are widely known. Over last few years, the usage of chlorine containing bleaching compounds has become limited

due to the formation of highly toxic chlorinated organic byproducts (AOX). Therefore chorine free bleaching agents like peracetic acid have gained attention as an alternative ecofriendly bleaching agent [10]. Hashem et al. [11] used chitosan-Mo and chitosan-Co complexes for the activation of peracetic acid and were able to obtain satisfactory results at low temperature of 70 ^{o}C. Replacement of hydrogen peroxide with other oxidizing agents, namely ammonium persulphate and potassium bromate was not successful. In contrast, the perborate did succeed but with lower efficiency when compared with hydrogen peroxide.

Cotton and other cellulosic fibres, conventionally, are dyed with direct, reactive, vat, reactive, azoic etc dyes, which are anionic in nature. Cotton also acquires negative surface charge when immersed in dye baths of above dyes leading to repelling action to them. To dissipate this -ve surface charge and to facilitate the dyeing, large amount of electrolytes such as common salt or Glauber's salt are added into the dye bath. These electrolytes and unexhausted dyes add to the pollution load when discharged through effluents. Thus attempts have been made to adopt salt free and alkali free dyeing by cationization of cotton by treatment with glycidyl trimethyl ammonium chloride, *N*, *N*-dimethyl azetidinium chloride, *N*-methylol acrylamide, chloropropionyl chloride etc. However, the question of ecological aspects arises here too [12]. Pretreatment of chitosan, due to its polycationic nature, has found to improve the direct dye uptake significantly and also reduce the salt consumption [6, 13]. Bandyopadhyay et al. [14] examined the effect of chitosan treatment on reactive dyeing of cotton. They reported decrease in salt requirement by 50% to produce a comparable shade to that of untreated fabric. The chitosan-treated fabric also showed improvement in fixation of reactive dyes. This result was explained by the increased exhaustion of negatively charged reactive dyes to the cotton, whose negative potential at the fiber surface was suppressed by the cationic chitosan treatment. Consequently, when alkali was added to the dye bath, a substantial quantity of dye was available for the reaction with cotton. It was also suggested that the amino groups of chitosan reacted with the reactive group in the dye and the fixation was further improved. The chitosan-treated fabric showed comparable color fastness properties to the untreated fabric. Lim and Hudson [15] used fibre reactive chitosan derivative containing quaternary ammonium group *O*-acrylamidomethyl-*N*-[(2-hydroxy

3-trimethylammonium) propyl] chitosan chloride (NMA-HTCC) for the treatment of cotton. They reported higher colour yield by cotton fabric when dyed with direct and reactive dyes without using salt. Kavitha et al. [16] studied the effect of chitosan treatment on natural dyeing of cotton namely turmeric. They reported increased tensile strength, flexural rigidity and shear strength. Cotton yarn coated with chitosan was found to be darker compared to uncoated yarn while dyeing for the same shade percentage. They reported the dyed yarn coated exhibited excellent activity against bacteria.

Often cotton fibres show small lightly colored or white spots due to presence of immature cotton fibers known as neps. Metha and Combs [17] evaluated nep coverage in the direct dyeing of cotton by the pretreatment of cotton with chitosan. The chitosan pretreatment was done by exhaust method. They reported by addition of sodium sulfate (Na_2SO_4) during the exhaust process improved the absorption of chitosan on cotton and fully covered the neps. The neps coverage was only partial when chitosan treatment was done in absence of salt. Further, the pretreatment was more effective for neps coverage in direct dyeing than reactive dyeing of cotton. Rippon [18] postulated that the affinity of chitosan to cotton would be by Van der Waals' forces due to the similar structures of chitosan and cotton. Another possibility mentioned for the binding chitosan to cellulose was cross linking by formation of Schiff base between cellulose's reducing end (−CHO) and the amino group of chitosan. In addition to the two possible bindings suggested by the authors, hydrogen bonding should also play an important role. Houshyar and Amirshahi [19] observed that the chitosan pretreatment increases the exhaustion of reactive dyes and the maximum dye up take was achieved by the fabric on which chitosan was applied by pad-dry cure method.

Though the literature does not explore the possible use of chitosan as pigment print thickener, it appears to be a good candidate, especially with the recent worldwide growth in the popularity of textile pigment printing [20-22]. They showed the prints of satisfactory colour fastness to rubbing, washing and light, however, the major problems were the poor colour value and undesired stiffness of the printed fabric. Tiwari and Gharia [23] attempted to use chitosan as a thickener in printing paste using various organic acids such as acetic, formic and oxalic acid respectively. They observed the chitosan unsuitable for print paste due very low viscosity and produce a high solid paste.

The rheology of pastes was reported to be pseudoplastic. Performance of the prints with respect to K/S, wash fastness, crock fastness and hand were observed to be unsatisfactory. Yuen et al.[24] studied the possibility of chitosan in preparing the pretreatment print paste for textile ink-jet printing. They employed a two bath method for the pretreatment of fabric with chitosan paste. The fabric was first treated with acidic chitosan solution by pad-dry cure (170 ^{0}C) method and then, in second stage, with alkaline bath containing sodium bicarbonate and urea. The two bath treated fabric was reported to give better colour yield when compared with chitosan treated and alginate treated fabrics.

Cotton fabric has a tendency for wrinkling when it is subjected to severe bending, which is attributed to the presence of free hydroxyl groups in the fibre molecules. The creasing problem is minimized by cross linking these free hydroxyl groups on adjacent molecules in the fibre using a suitable cross linking agent such as *N*-methylol compounds (UF, DMDHEU etc resins). However, these finishing agents suffer from one serious drawback of release of toxic free formaldehyde [25, 26]. As an alternative, on formaldehyde cross linking agents such as citric acid, butane tetra carboxylic acids (BTCA) etc are recommended. Among these, BTCA is most effective cross linking agent; but the cost is very high. Citric acid, although cheaper, is less effective and has drawback of yellowing problem due to the formation of unsaturated polycarboxylic acid (due to dehydration of citric acid). To counteract this yellowness, additives such as hydroxyethyl amines, borates or polyethylene glycols to citric acid bath are recommended. However, the process is still less effective [27]. The crease recovery power of citric acid can be improved satisfactorily by the incorporation of chitosan in presence of sodium hypophosphite monohydrate to the citric acid bath as reported by Waly and Okeil [28]. Here, the esterification reaction not only occurs between citric acid and cellulose but also between citric acid and hydroxyl groups of chitosan and the free carboxylic groups can also react with amino groups of chitosan by salt linkages. Tahlawy [29] studied the effect of chitosan in the finishing of cotton with citric acid in presence of sodium hypophosphite catalyst. He reported a recovery of losses (due to citric acid treatment) in dye uptake and tensile strength, and improved wrinkle recovery by the addition of chitosan in citric acid bath. The whiteness index, however, was deteriorated.

Authors proposed citric acid reacts with amino and hydroxyl groups of chitosan and hydroxyl groups of cotton through ester crosslinking or an inter-ionic attraction. Similar works were reported by several workers [30-32]. It is well known that the amino groups of chitosan readily react with aldehyde groups to form Schiff's base. This property of chitosan was employed by Bhattacharyya et al. [33] to scavenge free formaldehyde released from DMDHEU-finished cotton fabrics. They reported that the use of chitosan as an additive in DMDHEU finishing after dyeing was more effective in reduction of formaldehyde release as compared to the fabric which is chitosan-pretreated, dyed, and then DMDHEU-finished. The authors indicated that this result might be due to the blocking of the amino groups of chitosan by dye molecules on subsequent dyeing in the case of chitosan-pretreated cotton, and as a result, reduced reactions between chitosan and formaldehyde.

A major route towards the development of flame retardant cotton textiles has been the introduction of flame retardant materials containing nitrogen (N) and phosphorus (P) within the molecular structure of cellulose. Resin finishing with organophosphorus compounds such as THPC, THPC-APO, *N*- methylol dimethyl phosphonopropionamide seem to be most prevailing and reliable methods, but such treatments cause drop in tensile strength and skin irritation due to the liberation of formaldehyde [34]. Treatment of cellulosic based textiles with sodium stannate/phosphate to impart flame retardency is becoming one of the most interesting areas of research due to its non toxic, high durability, economically favourable, white colour and aesthetic properties [35]. Tahlawy et al.[36] incorporated chitosan in the phosphorylation bath as a nitrogen source. They reported that incorporation of 1% chitosan could reduce sodium stannate concentration to the one third of the amount that is used in the conventional process and hence the harsh feel of stannate was reduced. Thermogravimetric analysis of the treated fabric showed an increase in the residual percent of the fabric and decrease in both thermal degradation onset point (TDOP) and maximum degradation rate points as a function of stannate concentration. Increasing diammonium hydrogen phosphate from 2 to 10% in the finishing bath showed an increase in residue at 500 ^{0}C to 39.24%.

Chitosan and its derivatives exhibit good to excellent antibacterial and antifungal properties. The degree of deacetylation (DAC), molecular weight and concentration of

chitosan influence the antimicrobial activity [1]. Seong et al. [37] reported chito-oligosaccharide (DP 3 and 10) found to exhibit good antimicrobial activity and durability to washing without the need of crosslinking agent. The polycationic nature of chitosan is mainly responsible for the inhibition of bacterial and fungal growth. Fang et al. [38] reported that the chitosan inhibited growth of *Aspergillus niger* and induced considerable leakage of UV-absorbing and proteinaceous materials from it at pH 4.8 which was not induced at pH 7.6. Similarly, Tsai and Su [39] observed the chitosan-induced leakage of glucose and lactate dehydrogenase from *E. coli* cells and suggested that the death of cells resulted from the interaction between chitosan and the *E. coli* cell. The maximum antimicrobial activity exhibited by chitosan at acidic pH is also reported by other workers [40, 41]. The early work indicated that the antimicrobial effect was potent against a range of microbes, but the finishing was not durable. To improve durability, chitosan has been crosslinked to cotton using chemicals such as dimethylol dihydroxy ethylene urea (DMDHEU), 1,2,3,4-butane tetra carboxylic acid, citric acid or glutaric dialdehyde [30, 42]. These chemicals, some of which are used in durable press finishing of cotton, crosslink chitosan to cotton through hydroxyl groups. Ye et al.[43, 44] synthesized nanoscale core-shell particles of poly (n-butyl acrylate) core and chitosan shells and applied them to cotton fabric in a pad-dry -cure process. The antibacterial activity was maintained at over 90% reduction levels after 50 washes.

Chitosan has several beneficial applications in wool processing. One of the undesired properties of wool fibers is felting, which is the process of progressive entanglement of fibers under mechanical action in the presence of water i.e. directional frictional effect. The felting shrinkage results from the interlocking and hooking of contingent fibers due to the scales on the wool fibers [45, 46]. The scaly structure and the covalently bound fatty acids and the high amount of disulphide bridges make the outer wool surface (cuticle) highly hydrophobic and hence the diffusion of hydrophilic dyes and chemicals at and into the fibres is thus hindered [42]. Treatment of wool with chitosan has been found to reduce the felting problem. The bio-adhesive and cationic nature of chitosan enables it to form a strongly adhered film on individual fibres and prevent their entanglements [20]. Julià et al. [47] reported the peroxide pretreatment (alkaline or acidic) or oxidative plasma treatment could create new anionic groups such

as sulphonate and carboxylate which can improve the wettability of wool fibre and hence the binding power of chitosan. In another study of Julià's research group [48], they examined the effect of chitosan MW on the shrink-resistance of H_2O_2 pretreated (at pH 9.0) wool fabrics. The higher the molecular weight was, the greater the shrink resistance. However, such degradative treatments lead to considerable weight loss and damage to the fibre. Treatment of wool with a surfactant containing anionic groups can lead to higher pick up of chitosan causing no damage to the fibre. A combination of controlled enzymatic treatment followed by chitosan treatment can also give satisfactory antifelting effect. Further, these treatments have also shown increased shrink resistance and dyeability of wool towards reactive dyes [49]. Erpa et al. [50] reported the enhanced shrink resistance when air plasma treated wool is treated with chitosan. Jeong et al. [51] investigated the effect of chitosan treatment on changes in mechanical properties of wool due to pressure decatizing. They reported that the chitosan treatment increased the bending rigidity of fabric. The shear rigidity was also found to be increased but the tensile properties and frictional coefficient decreased. Okeil and Hakeim [52] conducted an experiment to give a pretreatment of chitosan to wool fabric to increase metal binding during the mordanting process with copper sulphate. The pretreated mordanted wool samples were successfully printed with natural dye, lawsone. Radetic et al. [53] investigated the possibility of improving the sorption of acid dyes from waste water using non woven material based on recycled wool. The woolen material was treated with low temperature air plasma and chitosan. These treatments were found to introduce new favourable functional groups and increased the active surface area. They reported the remarkably improved sorption properties of recycled wool for acid dyes for chitosan and plasma + chitosan treatment. Park et al.[54] investigated the antimicrobial and deodorant activities of chitosan treated wool fabric showed the chitosan of DAC above 70% good antibacterial and deodorant activity regardless of the molecular weight of chitosan.

Among synthetic fibres, polyester exhibits excellent properties such as elastic recovery, dimensional stability and blending compatibility with other fibres. However, polyester suffers from one serious drawback of hydrophobicity and consequently the static charge built-up problem. This static electricity is mostly responsible for dust/dirt attraction, sticking of clothes to human skin and uncomfortable feel, overlapping of fabric

on roller at plaiter end of stenter during heat setting process, malfunctioning of electric devices, sparks and ignition of its materials etc. To dissipate static charges, the fibre surface is coated with an antistatic agent, which is mostly synthetic hydrophilic resins, by simple pad-dry cure method. However, the effect is not durable [25]. An ecofriendly and durable antistatic finish can be obtained by the treatment of polyester with chitosan. Chitosan has the advantage that it shows high moisture regain even in low relative humidity and does not swell much in water. The finish is more stable on polyester that has under gone a caustic reduction treatment. Eom [55] treated polyester with chitosan in presence of malonic acid as a crosslinking agent between amino groups of chitosan and hydroxyl groups of polyester. Halim et al. [56] reported improved water uptake capacity of polyester and polyester/cotton blended fabrics by chitosan and monochlorotriazinyl -β-cyclodextrin treatments. They reported increased electrical conductivity and antistatic properties of finished fabrics.

In order to understand various properties of chitosan, different molecular weight chitosan derivatives were synthesized and applied on cotton fabric. The present chapter deals with the synthesis and characterization of chitosans of varying molecular weights, synthesized by hydrolytic degradation of high molecular weight chitosan using nitrous acid and subsequent applications of these chitosans to cotton fabrics. The molecular weights of chitosans were determined viscometrically using Ubbelohde capillary viscometer and Mark-Houwink equation. The viscosity behaviour of the synthesized chitosans was studied in presence and absence of electrolyte. The characterization of varying molecular weight chitosans was performed by FTIR analysis. The degree of deacetylation (DAC) was verified by ^{1}HNMR spectrum and elemental analysis.

The effects of applications of chitosan on dyeing and finishing properties of cotton were analyzed. Chitosans of varying molecular weights and concentrations were applied to cotton fabric by conventional pad-dry cure method. The surface morphology of treated fabric was examined under scanning electron microscope (SEM). Effect of such treatments on physical properties like appearance (in terms of whiteness, yellowness and brightness), stiffness, tenacity and water absorbency was evaluated. The chitosan was applied before and after dyeing of cotton, with direct dye and its effect on dyeing properties was examined. The effect of chitosan pre- treatment on the dyeability towards

acid dyes was also investigated. This biopolymer was used as a finishing agent with an intension to incorporate crease resistant property to cotton. The effect was compared with the commercially available wrinkle resistant agents and also examined its compatibility with them. The effect of different molecular weight chitosan treatment on antimicrobial properties was also evaluated using soil burial test as recommended by AATCC Test Method 30-2004.The work was further extended to the application of chitosan to cotton fabric by pad-dry-alkali treatment process.

2.2. MATERIALS AND METHODS

2.2.1 Fabric

100% cotton fabric (warp and weft count 40s, ends/in 142, picks/in 72 and fabric density: 125 g/m^2), at ready for dyeing stage, was procured from Mafatlal Industries Ltd, Nadiad, Gujarat State. All preparatory processes such as desizing, scouring, bleaching, mercerization etc were given in factory itself.

2.2.2 Dyes and chemicals

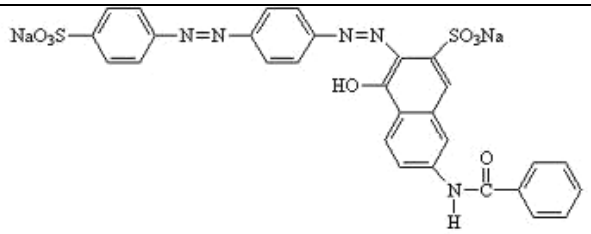
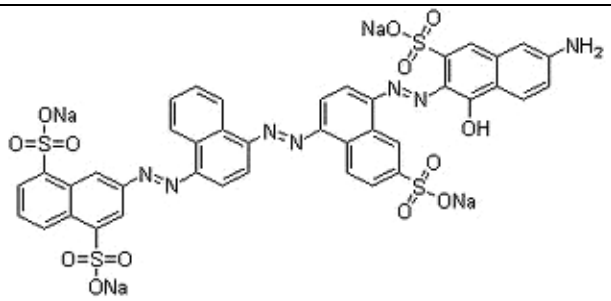
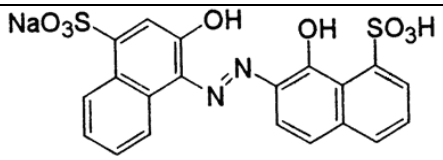
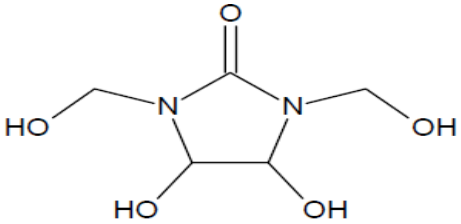
The details of various dyes and chemicals employed in present research investigation are given in Table 2.1. Other chemicals like acetic acid (CH_3COOH), sodium acetate (CH_3COONa), acetone (CH_3COCH_3), methyl alcohol(CH_3OH), sodium iodide (NaI), sodium hydroxide (NaOH), soda ash/sodium carbonate (Na_2CO_3), sodium sulphate (Na_2SO_4), sodium nitrite ($NaNO_2$), magnessium chloride ($MgCl_2$) etc used were of analytical grade obtained Qualikem Fine Chemicals Pvt Ltd, Vadodara. Anionic detergent (Ezee) was obtained from Godrej India Ltd. Double distilled water was employed for all synthesis and analytical purposes.

2.2.3 Purification of chitosan

Chitosan (1g) was dissolved in acetic acid solution (1.5 ml/L) using magnetic stirrer. The solution was filtered through filter fabric (mesh 128) to remove insoluble impurities. The filtrate was neutralized with sodium hydroxide solution to precipitate out the chitosan. The recovered chitosan was washed repeatedly with distilled water till neutral pH and then filtered. The precipitate was dewatered by treatment with methanol,

filtered and washed with acetone 3-4 times and then oven dried at 60 ^{0}C and stored in refrigerator.

Table 2.1 Specifications of various dyes and chemicals

Sr no	Name and Supplier	Specifications
1.	C.I.Direct Red 81 Colourtex Industries Ltd, Gujarat State, India.	 • Mol wt. 675.6
2.	C.I.Direct Blue 71 Colourtex Industries Ltd, Gujarat State, India.	 • Mol wt 1029.9
3.	C.I. Acid Blue 158 Colourtex Industries Ltd, Gujarat State, India.	 • Mol wt 495.45
6.	Chitosan • CHT MC (Marine Chemicals, Cochin, Kerala) • CHT (Mahtani Chitosan Pvt. Ltd., Veraval, Gujarat)	DAC 89.03%; Molecular weight 654,127; Viscosity 180 cPs, DAC 90%; Molecular weight 135,839; Viscosity 22 cPs.
7.	DMDHEU Mafatlal Industries Ltd, Nadiad, Gujarat State	Grade: Commercial, Active content: 40%, Chemical Formula: 

2.2.4 Synthesis of low molecular weight chitosan

Chitosans of different molecular weights were prepared by nitrous acid depolymerization method. A 2 % solution of chitosan in acetic acid (15 ml/L) and sodium acetate (10 g/L) was prepared. Predissolved dilute solution containing required amount of sodium nitrite was then added gradually to chitosan solution and stirred for two hrs at 30^{o}C to get desired viscosity level. The depolymerized chitosan was then precipitated out by caustic solution and washed to neutral pH with distilled water and then filtered. The precipitate was dewatered by treatment with methanol, filtered and washed with acetone 3-4 times and then oven dried at 60 ^{0}C and stored in refrigerator.Different grades of low molecular chitosan so prepared are listed in Table 2.8.

2.2.5 Fabric treatment with chitosan

Separate solutions of different molecular weight chitosan derivatives were made in solution containing acetic acid 15ml/L and sodium acetate 10 g/L and applied to fabric on a laboratory padding mangle (Model -PM0060388, R. B. Electronics & Engineering Pvt Ltd, Mumbai) with wet pick-up of 70% by two dip- two nip method (Mangle Pressure: 20 psi, Speed: 3 m/min). After drying the fabric samples were cured in oven at 150 ^{0}C for 4 min. The samples were then washed in the following sequence:

Hot wash (Twice) [85 ^{0}C /20mins] $\rightarrow$ Alkali wash [Soda ash 1 g/L, MLR 1:50] $\rightarrow$ Hot wash $\rightarrow$ cold wash $\rightarrow$Dry.

2.2.6 Application of chitosan by pad-dry-alkali process

Cotton fabric was soaked for 30 minutes in chitosan solution prepared with solution containing acetic acid 15ml/L and sodium acetate 10 g/L. The fabric was then passed through a laboratory padding mangle (Model-PM0060388, R. B. Electronics & Engineering Pvt Ltd, Mumbai) with wet pick-up of 70% by two dip- two nip method (mangle pressure 20 psi, speed 3 m/min) and air dried. The sample was then dipped in sodium hydroxide solution (1 g/L) for 15 minutes, washed thoroughly until neutral pH, dried and hot pressed.

2.2.7 Dyeing with direct dyes

The cotton fabric was dyed with direct dye (1% o.w.m.) in presence of Glauber's salt (20% o.w.m.) and soda ash (5% o.w.m.) at pH 10.9 and temperature 90 ^{0}C for 60 minutes on water bath. The material- to- liquor ratio was maintained at 1:40. The dyed sample was then rinsed with cold water 3 times, air dried and hot pressed.

The dyed samples were evaluated for colour strength in terms of K/S values on computer colour matching system namely Spectroscan 5100A (Premier Colorscan, Mumbai, Maharastra, India) using Kubelka-Munk equation (2.1). The readings were taken for the average of four scans.

$$K/S = \frac{(1-R)^2}{2R} \qquad \textbf{(2.1)}$$

Where, K is absorption coefficient, S is scattering coefficient and R is reflectance.

The washing fastness of dyed samples was evaluated according to ISO1. The test was carried out in Launder-o-meter (R.B. Electronics, Vapi, Gujarat). The dyed specimen (10 X 4 cm), sandwiched between undyed cuttings of same material, was treated with detergent solution containing: detergent (Ezee detergent, Godrej) 0.5 % w/v at 40 ^{0}C for 30 minutes. The material- to- liquor ratio was maintained at 1:40. The sample was taken out, rinsed, air dried and hot pressed. The fastness ratings were assessed using SDC grey scale for change in colour (ISO 105A02, 1993: BS EN 20105 A02, 1995).

The rubbing fastness of dyed samples was determined according to AATCC test method 8-2005.The dyed test specimen was placed on the base of the crockmeter (Paramount crockmeter) along the warp. Rubbing was carried out, to and fro, along a straight line 10 cm long, 10 times and for 10 sec with rubbing finger (under 900g wt) clamped with dry white cotton cloth. Staining was assessed by comparing with grey scale for assessing staining (ISO 105A03, 1993: BS EN 20105 A03, 1995).

2.2.8 Dyeing with acid dye

The fabric sample was dyed with acid dye (2% o.w.m.) at 90 ^{0}C for 60 minutes from a dye bath containing acetic acid (1 ml/L) at pH 3.8. The dyed sample was then

rinsed with cold water, air dried and hot pressed. The dye up take was evaluated in terms of K/S values using equation 2.1.

2.2.9 Determination of tenacity

The tenacity and elongation of treated and untreated cotton fibres were measured on Stelometer (SITRA, Coimbatore, India). The breaking load (kg) and elongation at break were obtained directly from scale. The samples were then collected and weighed. The tenacity (average of 5 readings) was calculated using following formula.

$$\text{Tenacity (g/tex)} = \frac{\text{Breaking Load (kgs)} \times 1.5 \times 10}{\text{Sample Weight (mg)}} \quad \textbf{(2.2)}$$

Sample Length = 1.5 cm

2.2.10 Determination of viscosity

The molecular weight and viscosity behaviour of chitosan was determined using Ubbelohde capillary viscometer (No 1A) at 30 ^{o}C having flow time for distilled water, $T_{0=}$15.57 seconds. Chitosan solutions of different concentrations in 0.25M acetic acid and 0.25M sodium acetate were prepared. During preparation, all the solutions were magnetically stirred for 1 hour to ensure proper dissolution of chitosan and were filtered using Whatman filter paper no 4. The flow time of chitosan solutions at different concentrations and of the solvent was recorded in triplicate and the average value was calculated. The intrinsic viscosity [η] was calculated graphically by extrapolating the curve of reduced viscosity Vs concentration to zero concentration. The molecular weight was then calculated by using Mark-Houwink equation **(**2.5) [57].

2.2.11 FTIR analysis

FTIR of chitosan samples were taken on a Thermo Nicolet iS10 Smart ITR spectrophotometer (Thermo Fisher Scientific, USA), equipped with an OMNIC-Software, a DTGS detector, and a Ge-on-KBr beamsplitter (4000–500 cm^{-1}). The FT-IR ATR spectra (32 scans, 4 cm^{-1} resolution) were recorded using a single reflection

horizontal ATR accessory with a spherical ZnSe crystal fixed at an incident angle of 45^{o}. A sample with a 2-mm diameter was measured.

2.2.12 ^{1}H-NMR spectroscopy

The ^{1}H-NMR spectra of chitosan in D2O were obtained by using a Bruker Avance 400 spectrometer (USA), at a resonance frequency of 400 MHz using Topspin1.3 software. The ^{1}H-NMR spectra were performed at a temperature of 25 °C. Test was performed at Dept. of Chemistry, S.P. University, Vallabh Vidyanagar, Gujarat.

2.2.13 Elemental analysis

The carbon, hydrogen and nitrogen content of chitosan samples were estimated by using CHN/S/O analyzer Perkin Elmer, Series II, 2400. Test was performed at Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Gujarat.

2.2.14 Scanning electron microscopy

Treated and untreated fabric samples were fixed on carbon coated aluminium sheets and then were observed under scanning electron microscope (Model JSM5610LV, version 1.0. Joel, Japan) in vacuum. Test was performed at Dept of Metallurgy, Feculty of Tech and Engg, Vadodara, Gujarat.

2.2.15 Evaluation of indices

The samples were evaluated on Spectroscan 5100A (Premier Colorscan, Mumbai, India) for whiteness index (WI) (10 deg/D65/Hunterlab), yellowness index (YI) (2 deg/C/ASTM D 1925), brightness index (BI) (2 deg/C/TAPPI 452/ISO 2470). The readings were taken for the average of four scans.

2.2.16 Evaluation of stiffness of fabric

Stiffness of the fabric sample (27 X 200 mm) in terms of bending length was measured as per standard ASTM D 1388-996 (Prolific stiffness tester, Prolific Engineers, Noida, UP, India). The readings were taken for the average of four measurements.

2.2.17 Evaluation of absorbency of fabric

Absorbency of treated and untreated cotton fabrics were evaluated by drop penetration method as per AATCC test method 79-2000. The fabric was mounted on embroidery ring and a drop of water was placed on it using burette. The time required for complete absorption of water drop was measured using stop watch. The absorbency was recorded for the average of nine readings.

2.2.18 Determination of crease recovery angle of fabric

Crease recovery angles were measured as per AATCC test method 66- 2003. The test specimen (26 X 52 mm) was folded (26 X 26 mm) and loaded under 500 g weight for 5 minutes to create a folded angle (crease). The specimen was then suspended in crease recovery tester (SASMIRA, Mumbai, India) for 5 minutes for a controlled recovery and then the recovery angle was examined. The total of crease recovery angle (CRA) measured for warp way and weft directions was considered. The average of two readings was recorded.

2.2.19 Soil burial test

The untreated and treated samples were subjected to soil burial test as per AATCC Test Method 30-2004. The standard soil for the burial test was prepared by mixing Garden soil 50 parts, cow dung 20 parts and water 30 parts and allowed to ferment for one month. The compost soil was covered with polythene paper to prevent the evaporation of moisture.

The treated and untreated cotton fabrics (15 X 4 cm) were incubated in the compost soil bed at 30±2°C for a stipulated period of five days. The specimen were then washed with water and dried in air and tested for strength measurement (tenacity) on stelometer (SITRA, Coimbatore, India) using equation 2.2.

2.3. RESULTS AND DISCUSSION

Two different grades of chitosan namely CHT and CHT-MC having viscosities 22 and 180 cPs respectively and almost similar degree of deacetylation (DAC) values (90%) were employed for the present investigation. The purified samples were analysed for

FTIR spectroscopy and ^{1}H NMR spectroscopy for structural characterization. The DAC values were verified from ^{1}H NMR spectra and CHN analysis. Molecular weights were determined viscometrically.

2.3.1 FTIR spectroscopy

The structural characterization of CHT and CHT-MC was done by FTIR spectra analysis, which is presented in Figure 2.1 and Figure 2.2. The spectra of these two samples were found to be almost similar indicating that both the samples possessing same structural features. In the spectra, the region above 1500 cm^{-1} wavenumber is commonly known as 'functional group region' to identify functional groups such as primary amine, alcohols, methylene groups etc. Another region which is below 1500 cm^{-1} wavenumber known as 'finger print region' referred to characterize the saccharide backbone [58].

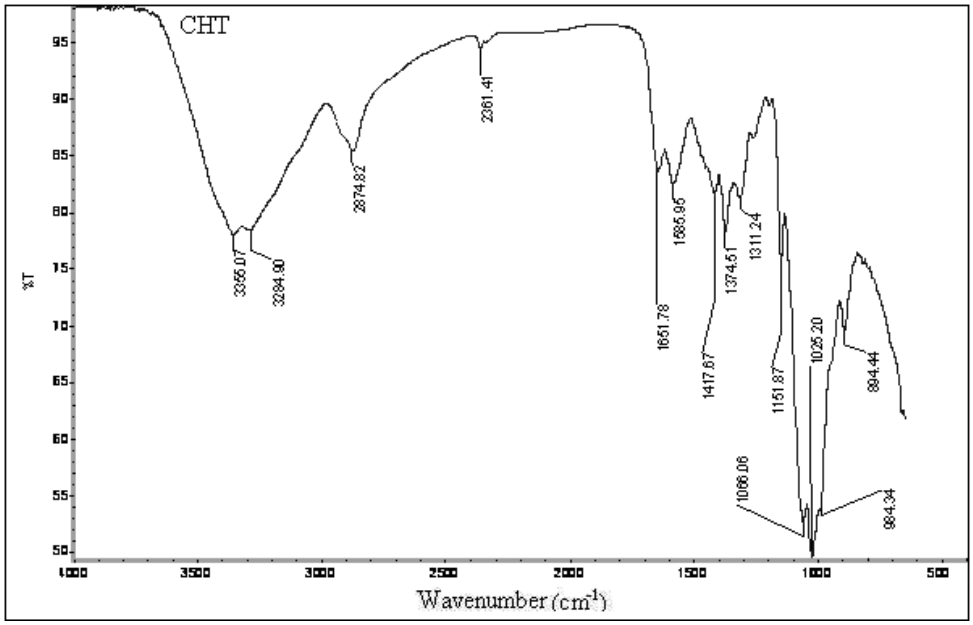


Figure 2.1 FTIR spectrum of CHT

A broad band observed at wavenumber around 3355 cm^{-1} is mainly attributed to O-H, NH and NH_2 stretch [59-61] and the absorption peak in region 2864 to 2874 cm^{-1} is due to the C-H symmetrical and unsymmetrical stretch. The absorption band at 1651 cm^{-1} is assigned to C=O (carbonyl) stretching of secondary (amide I) amide group, which is characteristic of *N*-acetyl group and the medium peak at 1585 cm^{-1} is due to bending

vibrations of N-H of amide II bond (*N*-acetyl residue) and the primary amine[59, 60]. The corresponding peaks of CHT-MC in Figure 2.2 are 1650 and 1572 cm^{-1} respectively. Another medium absorption peak at 1374 to 1376 cm^{-1} characterizes the N-H of amide III bonds [60]. Absorption peaks at wave numbers 1151, 1066, 984 and 895 cm^{-1} are assigned to secondary hydroxyl groups (-CH-OH) due to C-O bending in cyclic alcohols or saccharide structure [59-61]. A strong absorption peak at 1025 cm^{-1} is due to 1^{o} hydroxyl group, characteristic peak of $-CH_2OH$ in primary alcohols, arised from C-H bending [60]. Also, various bending vibrations of C-O at different peaks like 894 and 1151 cm^{-1} in fingerprint region characterize the saccharide structure.

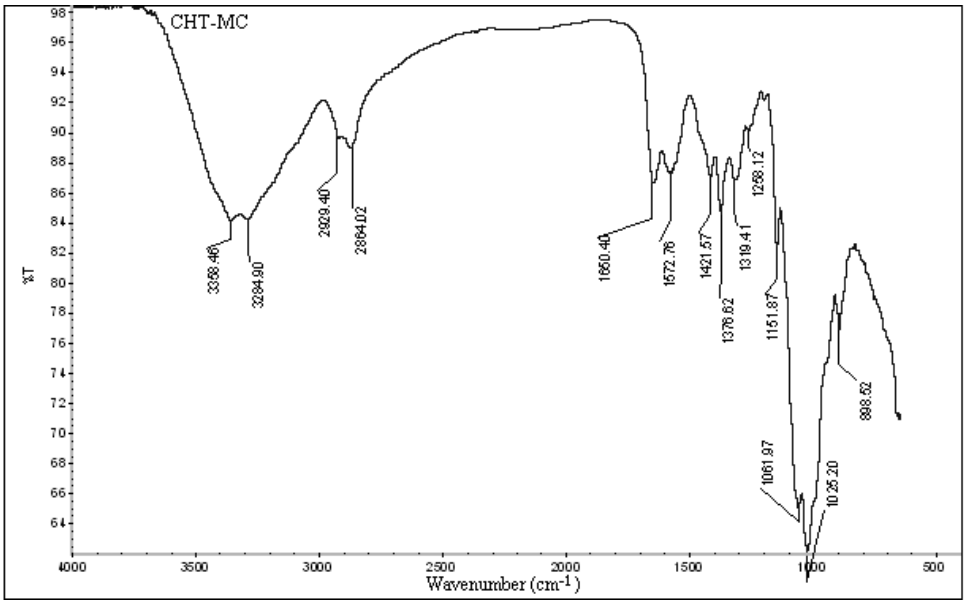


Figure 2.2 FTIR spectrum of CHT-MC

2.3.2 ^{1}H-NMR Spectroscopy

The ^{1}H-NMR spectra have been extensively used in quantitative determination of degree of deacetylation (DAC, %), degree of quaternization (DQ, %), degree of substitution (DS, %) etc properties of chitosan due to its reliability and is shown to cause no degradation of polymer [62-64]. It can be observed from the spectrum of CHT (Figure 2.3) that the signal (chemical shift, δ) at 3.114 ppm corresponds to the hydrogen bonded to the carbon atom C2 of the glucosamine ring and the integral (I_{H2}) is 3.66. The peak at δ=1.964 ppm corresponds to acetyl group (i.e. H of methyl group of acetamido moiety)

with intensity (I_{NAc}) 1.01. While the signals between 3.30 and 4.00 ppm correspond to the hydrogen atoms bonded to carbons C3, C4, C5 and C6 of the glucopyranose units. The signal for anomeric protons H1 (the anomeric protons of the D-glucosamine units) and H1' (the anomeric protons of the *N*-acetyl D- glucosamine units) respectively are traced at peaks δ= 4.67 and 5.423 ppm respectively having the intensities (I_{H1}) 1.03 and ($I_{H1'}$) 0.73 respectively.

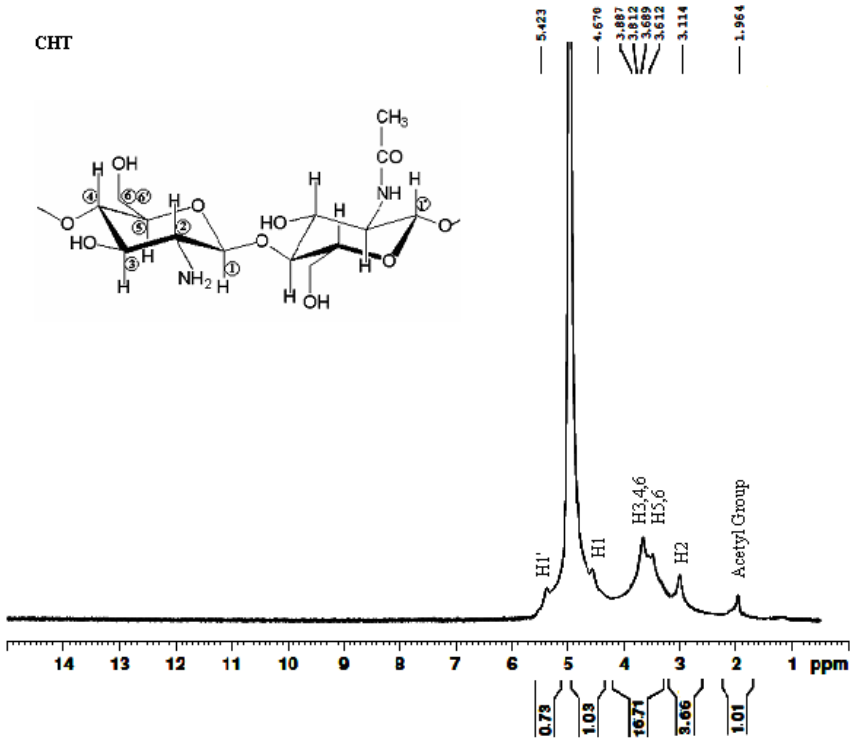


Figure 2.3 ^{1}H NMR spectrum of CHT

From the signal integrals of ^{1}H-NMR spectrum, the degree of deacetylation (DAC, %) can be evaluated by using following equation (2.3).

$$\text{DAC (\%)} = \left(1 - \frac{1/3\,(\text{Signal intensity due to acetyl group, } I_{NAc})}{(\text{Signal intensity due to H of C2, } IH_2)}\right) \times 100 \qquad \textbf{(2.3)}$$

I_{NAc} = δ at 1.964 ppm = 1.01

I_{H2} = δ at 3.114 ppm = 3.66

$$\text{DAC} = \left(1 - \frac{1/3\,(1.01)}{(3.66)}\right) \times 100 = 90.80\ \%$$

2.3.3 Elemental analysis

Elemental analysis for carbon, nitrogen, oxygen, hydrogen etc of chitosan and its derivatives can be a useful tool for the determination of parameters like degree of deacetylation (DAC value) [65, 66]. The DAC value of chitosan can be calculated from the equation (2.4)

$$\frac{C1}{N1} \times (1 - D) + \frac{C2}{N2} \times D = \frac{C3}{N3} \qquad \textbf{(2.4)}$$

Where, D is degree of acetylation. C1/N1 is calculated from the formula of glucosamine residue, C2/N2 from the *N*-Acetyl Glucosamine residue and C3/N3 is found value of sample by elemental analysis.

The empirical formula of chitosan can be written as $(C_6H_{11}NO_4)_{1-D}$ $(C_8H_{13}NO_5)_D$, from which the CHN values and C/N values can be determined as follows.

Glucosamine	C1 (%)	H1 (%)	N1 (%)	C1/N1
	44.72	6.83	8.70	5.14
N- Acetyl glucosamine	C2 (%)	H2 (%)	N2 (%)	C2/N2
	47.29	6.40	6.89	6.86

C3/N3 value is determined from elemental analysis of chitosan samples as follows.

Sample	C3 (%)	H3 (%)	N3 (%)	C3/N3
CHT	35.52	6.75	6.67	5.325
CHT-MC	35.40	6.80	6.68	5.30

Theoretical values calculated from empirical formula of chitosan (DAC 90%): C45.04%, H 6.78%, N 8.47% and C/N 5.32

Calculations:

Determination of DAC of CHT

Substituting respective C/N values in equation (2.4), the value of degree of acetylation (D) and from which the DAC value can be calculated.

$$\frac{C1}{N1} \times (1-D) + \frac{C2}{N2} \times D = \frac{C3}{N3}$$

$$5.14\,(1-D) + 6.86 \times D = 5.325$$

D = 0.1076 or 10.76%

DAC of CHT = 100-10.76 = 89.24 %.

Similarly, the DAC value for CHT-MC was obtained as 90.7 %. The DAC values obtained from various analytical methods such as ^{1}HNMR spectroscopy and elemental (CHN) analysis were in close agreement with the data provided by the supplier as summarized in Table 2.2. Therefore for a common DAC value of 90% was taken for all the calculations whenever required hereafter.

Table 2.2 Degree of deacetylation of parent chitosan samples

Sample code	**Degree of deacetylation, %**		
	Manufacturers' data	**^{1}HNMR method**	**Elemental analysis method**
CHT	90	90.8	89.24
CHT-MC	89.03	-	90.7

2.3.4 Studies on determination of viscosity average molecular weight of chitosan

The viscosity of polymer solution, at the molecular level, is a direct measure of the hydrodynamic volume of the polymer molecules which in turn is governed by the molecular size or chain length and hence the molecular weight [67, 68].Therefore the viscosity, measured by capillary viscometer, is widely employed to determine the average molecular weight of a polymer by using the famous Mark-Houwink equation (2.5).

$$[\eta] = k\,[M_V]^{\alpha} \qquad \textbf{(2.5)}$$

Where M_V is the viscosity average molecular weight of polymer, α and k are constants (α = 0.83 and k = 1.4 X 10^{-4} for 0.25M acetic acid and 0.25M sodium acetate

solvent system) [57] and [η] is the limiting viscosity number or intrinsic viscosity and can be determined from the Huggins equation (2.6) [68].

$$[\eta] = \lim_{c \to 0} (\eta - \eta_s)/ \eta_s C \quad \textbf{(2.6)}$$

Where η is the viscosity of solution and η_s is the viscosity of solvent and C is the concentration. As indicated in equation (2.6), when $(\eta - \eta_s)/ \eta_s C$ i.e. reduced viscosity (η_{red}) is plotted against concentration (C), the intercept to Y-axis corresponds to intrinsic viscosity [η].

In general, the viscosity average molecular weight (Mv) of chitosan was determined using Ubbelohde capillary viscometer by measuring the flow time (T) of chitosan solutions at varying concentrations (C) through the determination of reduced viscosity and intrinsic viscosity as shown in Table 2.3 using equations 2.7, 2.8 and 2.9 and Figure 2.4, and using Mark-Houwink equation (2.5). The calculated molecular weights of CHT and CHT-MC are shown in Table 2.8.

Relative viscosity: $\eta_{rel} = \frac{T}{T_0}$ **(2.7)**

Specific viscosity: $\eta_{sp} = \eta_{rel} - 1$ **(2.8)**

Reduced viscosity: $\eta_{red} = \frac{\eta_{sp}}{C}$ **(2.9)**

Table 2.3 Viscometric analysis of chitosan solution

Conc (C) g/dL	CHT-MC				CHT			
	Flow time (T), Sec	**Relative viscosity (η_{rel})**	**Specific viscosity (η_{sp})**	**Reduced viscosity (η_{red})**	**Flow time (T), Sec**	**Relative viscosity (η_{rel})**	**Specific viscosity (η_{sp})**	**Reduced viscosity (η_{red})**
0.05	23.77	1.49	0.49	10.21	-	-	-	-
0.1	34.63	2.18	1.18	11.82	21.27	1.34	0.34	3.4
0.15	46.65	2.94	1.94	12.93	-	-	-	-
0.2	58.79	3.71	2.71	13.52	28.27	1.78	0.78	3.91
0.25	76.81	4.84	3.84	15.36	-	-	-	-
0.3	98.90	6.23	5.23	17.44	37.23	2.35	1.35	4.49
0.4	143.91	9.07	8.07	20.17	49.14	3.10	2.10	5.24
0.5	217.25	13.69	12.69	25.38	62.61	3.95	2.95	5.89
0.6	330.75	20.84	19.84	33.03	78.69	4.96	3.96	6.60
0.7	-	-	-	-	98.32	6.20	5.20	7.42
0.8	-	-	-	-	125.28	7.89	6.89	8.62
0.9	-	-	-	-	157.41	9.92	8.92	9.91
1.0	-	-	-	-	196.00	12.35	11.35	11.35

Solvent: Acetic acid 0.25M, sodium acetate 0.25M, T_0 15.87 sec

Calculations

The intrinsic viscosities[η] of CHT and CHT-MC, from Figure 2.4, were determined to be 2.55 and 9.5 respectively.

Mark-Houwink equation, $[\eta] = k [M_V]^{\alpha}$ **(2.5)**

Where, $\alpha = 0.83$ and $k = 1.4 \times 10^{-4}$ for 0.25M acetic acid and 0.25M sodium acetate solvent system

(1) Molecular weight of CHT

Intrinsic viscosity, $[\eta] = 2.55$

$2.55 = 1.4 \times 10^{-4} M^{0.83}$

$M_V = 135,839$

(2) Molecular weight of CHT-MC

Intrinsic viscosity, $[\eta] = 9.4$

$9.4 = 1.4 \times 10^{-4} M^{0.83}$

$M_V = 654,127$

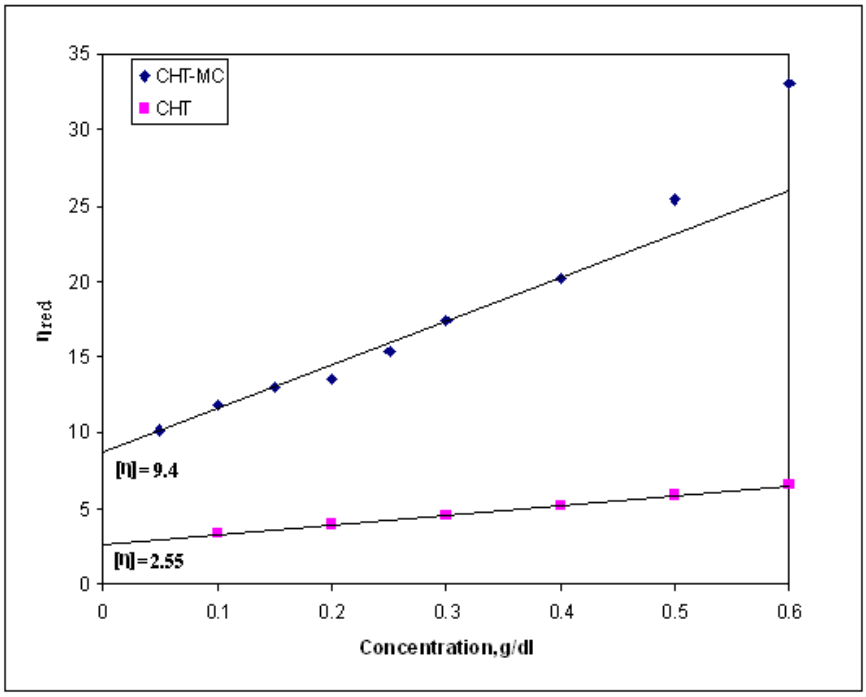


Figure 2.4 Intrinsic viscosity determination of chitosan

2.3.5 Depolymerization of chitosan for synthesizing low molecular weight chitosans

Chitosan is characterized mainly by two variables, namely, degree of deacetylation and the molecular weight. Degree of deacetylation determines the number of free amino groups present in the chitosan macromolecule, which in turn determines the functionality/reactivity, polarity and water solubility of the polymer. On the other hand, molecular weight determines the strength of its fiber/film and viscosity of its solution [2, 69]. The molecular weight of chitosan depend on the source of precursor chitin and deacetylation conditions (time, temperature, and concentration of NaOH), respectively. The molecular weight of most of native chitosan, obtained from deacetylation of crustacean chitin, may be of the order 10^5 to 10^6 [69], which may be very high for the textile applications as they produce highly viscous solutions. Consequently, for ease of applications, it is necessary to reduce the molecular weight to much lower value. Various methods controlled depolymerization have been proposed to obtain chitosan of desired molecular weights.

Chitosans of desired molecular weight can be obtained by controlled depolymerization by methods such as acid hydrolysis (HCl, H_2SO_4, HNO_2 etc) [28, 37,

70-72], free radicals (H_2O_2, $K_2S_2O_8$) [73], enzymatic [72, 74], radiations (UV, γ rays) [75, 76], ultrasound [77], microwave and thermal treatments [78]. In physical methods, Baxter et al. [77] studied the effect of ultrasonication on the degradation of chitosan. They found that intrinsic viscosity of samples decreased exponentially with increasing sonication time and rates of intrinsic viscosity decreased linearly with ultrasonic intensity. Choi et al. [76] investigated the depolymerization of chitosan using irradiation with different doses (2~200 kilograys) of gamma rays. Their results showed that viscosity of irradiated chitosan rapidly decreased with increasing irradiation dose.

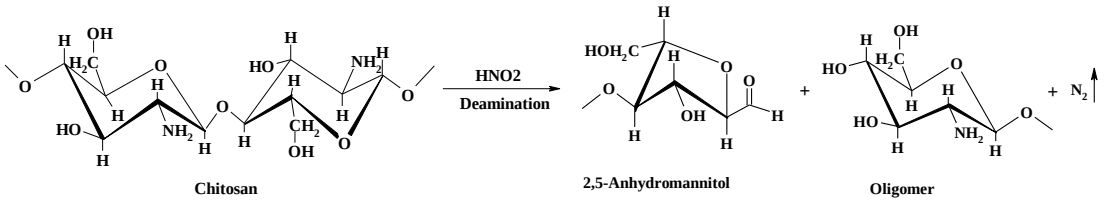
Feng Tian et al.[73] reported the method for depolymerization of chitosan by hydrogen peroxide and their IR and ^{1}HNMR studies confirmed the depolymerization leading to breakage of 1-4 -β-D- glucoside bonds of chitosan. They proposed the attack of per hydroxyl radical ($HO^{\cdot}$), generated from the H_2O_2 decomposition, at amino group leading to hydrogen abstraction. The resulting unstable glucosamine radical in presence of water leads to rupture of adjacent glucosidic linkage. They also proposed that the depolymerization in crystalline region mainly takes place at the surface by peeling-off process while the amorphous region is depolymerized by penetrating pattern. Trzcinski [75] employed the combined degradation of chitosan using hydrogen peroxide and UV light for the enhanced degradation rate. Photochemical degradation by means of UV light also undergoes as a result of free radical reactions along the macromolecules. Kabal'nova et al.[79] employed the ozonation of chitosan in dilute acid solution and showed a remarkable decrease of molecular mass of polysaccharide in proportion to reaction time or amount of applied ozone. According to Demin et al. [80], the initial stage of the interaction of ozone with polysaccharide is its electrophilic attack on C(1)-H bond with the formation of labile hydrotrioxides, destruction of which results in depolymerization of polysaccharide

Enzymatic degradation of chitosan polymer is possible to get low molecular weight chitosan. Enzymatic process has the advantage of its specificity and the ease in the fractionation of product [81]. Lee et al.[74] used commercial bromelain for the partial depolymerization of chitosan. The enzymatic reactions were determined by the liberation of reducing sugar and the reduction in viscosity. They proposed/recommended 7% w/w enzyme treatment for 2h at pH 5 for the satisfactory results. Ilyina et al [82] reported

chitinase and chitosanase as most effective enzymes, which are found in fungus, bacteria and plants, to hydrolyze chitosan. Other enzymes such as glucosanase, lipase, tannase and protease were found to have chitosanolitic activities, as reported by Yalpani and Pantaleone [81].

Nitrous acid method for the oxidative depolymerization of chitosan has been well documented [28, 37, 52, 83]. When chitosan solution is treated with nitrous acid, produced from acidic sodium nitrite it undergoes deamination reaction with subsequent cleavage of β- glycosidic linkages. Mao et al. [83] reported a large series of chitosans with desired molecular weights could be obtained by changing chitosan/$NaNO_2$ molar ratio, chitosan initial concentration and reaction time. The molecular weight of the depolymerized chitosan was linear with chitosan/$NaNO_2$ ratio. The reproducibility of this method was fairly good. The overall stoichiometry of the reaction between chitosan and nitrous acid (HONO) is shown scheme 2.1. Nitrosating species originating from HONO attack the amino groups and subsequently cleave the β- glycosidic linkages to produce low molecular weight product and 2,5-anhydro-D-mannose is formed as the reducing end group of the cleaved polymer [28, 37, 52].

$$NaNO_2 + H^+ \longrightarrow HNO_2 + Na^+$$



Scheme 2.1 Depolymerization of chitosan by nitrous acid

On account of these advantages and its better control on the extent of depolymerization nitrous acid method was used to depolymerize chitosan in this study. Most of the low molecular weight chitosan derivatives namely CHT-D2, D3, D4 and D5 were derived from the starting material CHT whereas CHT-D1 was obtained from CHT-MC. During depolymerization process, parameters like chitosan concentration (2 % w/v),

acetic acid (15 ml/L), sodium acetate (10 g/L), temperature (30 ^{o}C) and treatment time (2h) was kept constant and the concentration of sodium nitrite was varied as shown in Table 2.4. The viscosity measurements data, determined using equations 2.7, 2.8 and 2.9 of low molecular weight chitosan derivatives produced from depolymerization of CHT and CHT-MC are presented in Table 2.5, Table 2.6 and Table 2.7. The intrinsic viscosities of depolymerised chitosan were determined from the plots of reduced viscosity against concentration of chitosan as shown in Figure 2.5 and the molecular weights of chitosan derivatives produced from depolymerization of CHT and CHT-MC are summarized in Table 2.8.

Table 2.4 Syntheses of low molecular weight chitosan derivatives

Sample code	Parent chitosan	Sodium nitrite, %
CHT-D1	CHT-MC	0.10
CHT-D2	CHT	0.5
CHT-D3	CHT	1.25
CHT-D4	CHT	2
CHT-D5	CHT	3.1

Conc: CHT-MC 10 g/L and CHT 20 g/L, Treatment time 2h,
Sodium nitrite conc was taken on the percentage of parent chitosan, temp 30 ^{o}C

Table 2.5 Viscometric analysis of CHT-D1 and CHT-D2 solutions

Conc (C), g/dL	CHT-D1				CHT-D2			
	Flow time (T), Sec	Relative viscosity (η_{rel})	Specific viscosity (η_{sp})	Reduced viscosity (η_{red})	Flow time (T), Sec	Relative viscosity (η_{rel})	Specific viscosity (η_{sp})	Reduced viscosity (η_{red})
0.1	25.73	1.621	0.621	6.21	18.44	1.162	0.162	1.62
0.2	40.50	2.552	1.552	7.76	21.46	1.352	0.352	1.76
0.3	60.00	3.781	2.781	9.27	24.96	1.573	0.573	1.91
0.4	84.49	5.324	4.324	10.81	28.50	1.796	0.796	1.99
0.5	112.92	7.115	6.115	12.23	33.01	2.080	1.080	2.16
0.6	147.37	9.286	8.286	13.81	37.29	2.350	1.350	2.25
0.7	203.28	12.809	11.809	16.87	42.98	2.708	1.708	2.44
0.8	268.90	16.944	15.944	19.93	48.37	3.048	2.048	2.56
0.9	352.38	22.204	21.204	23.56	54.86	3.457	2.457	2.73
1.0	424.68	26.760	25.760	25.76	61.26	3.860	2.860	2.86

Solvent ingredients: Acetic acid 0.25M, sodium acetate 0.25M, T_0= 15.87 sec

Table 2.6 Viscometric analysis of CHT-D3 and CHT-D4 solutions

Conc (C), g/dL	CHT-D3				CHT-D4			
	Flow time (T), Sec	Relative viscosity (η_{rel})	Specific viscosity (η_{sp})	Reduced viscosity (η_{red})	Flow time (T), Sec	Relative viscosity (η_{rel})	Specific viscosity (η_{sp})	Reduced viscosity (η_{red})
0.1	17.37	1.095	0.095	0.95	16.74	1.055	0.055	0.55
0.2	19.08	1.202	0.202	1.01	17.65	1.112	0.112	0.56
0.3	21.15	1.342	0.342	1.11	18.57	1.170	0.170	0.57
0.4	22.98	1.448	0.448	1.12	19.62	1.236	0.236	0.59
0.5	25.03	1.577	0.577	1.15	20.73	1.307	0.307	0.61
0.6	27.30	1.720	0.720	1.20	21.77	1.372	0.372	0.62
0.7	29.67	1.869	0.869	1.24	22.98	1.448	0.448	0.64
0.8	32.25	2.032	1.032	1.29	24.12	1.520	0.520	0.65
0.9	35.29	2.224	1.224	1.36	25.25	1.5913	0.5913	0.66
1.0	37.93	3.391	2.391	1.39	26.67	1.681	0.681	0.68
1.2	-	-	-	-	28.86	1.818	0.818	0.68
1.6	-	-	-	-	36.17	2.216	1.216	0.76
2.0	-	-	-	-	41.90	2.640	1.640	0.82

Solvent ingredients: Acetic acid 0.25M, sodium acetate 0.25M, T_0= 15.87 sec

Table 2.7 Viscometric analysis of CHT-D3 and CHT-D4 solutions

Conc (C), g/dL	CHT-D5			
	Flow time (T), Sec	Relative viscosity, (η_{rel})	Specific viscosity, (η_{sp})	Reduced viscosity, (η_{red})
0.1	16.43	1.035	0.035	0.35
0.2	17.02	1.072	0.072	0.36
0.3	17.63	1.111	0.111	0.37
0.4	18.30	1.153	0.153	0.38
0.5	18.96	1.195	0.195	0.39
0.6	19.70	1.241	0.241	0.40
0.7	20.44	1.288	0.288	0.41
0.8	21.20	1.336	0.336	0.42
0.9	22.00	1.385	0.385	0.43
1.0	22.87	1.441	0.441	0.44

Solvent ingredients: Acetic acid 0.25M, sodium acetate 0.25M, T_0= 15.87 sec

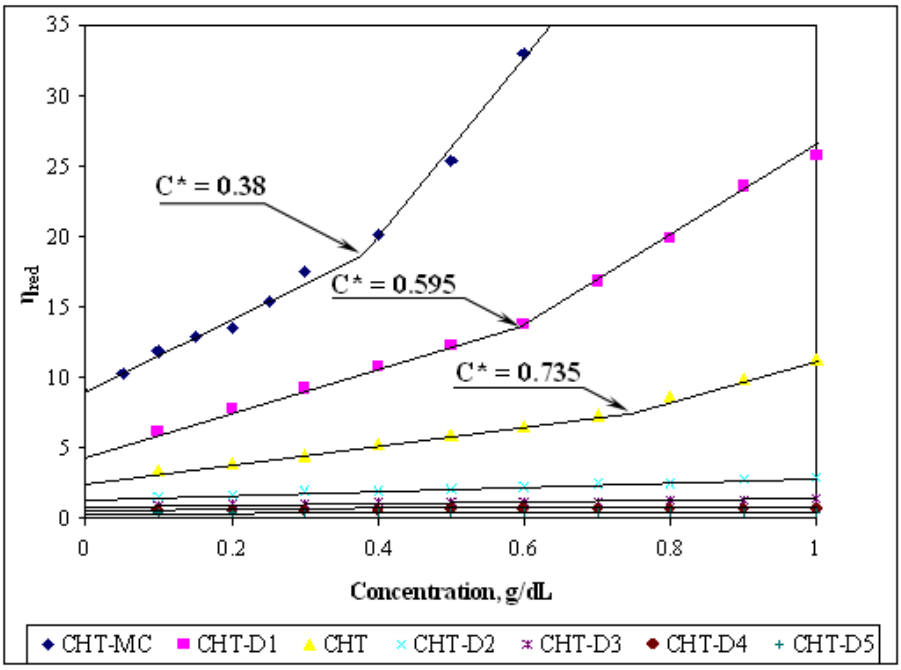


Figure 2.5 Intrinsic viscosities of different grades of chitosan solutions

Table 2.8 Intrinsic viscosity and viscosity average molecular weights of different grades of chitosan

Chitosan	Intrinsic Viscosity [η]	Molecular Weight, Mv	Overlap concentration (C*), g/dL
CHT-MC	9.40	654,127	0.38
CHT-D1	4.72	285,231	0.595
CHT	2.55	135,839	0.735
CHT-D2	1.50	71,676	-
CHT-D3	0.91	38,733	-
CHT-D4	0.535	20,698	-
CHT-D5	0.34	11,986	-

It is envisaged from Figure 2.6 and Figure 2.7 that the IR spectra of chitosan and depolymerised chitosan are almost similar which indicates that the process of depolymerisation caused no chemical change in the structure of the polymer except reduction in molecular weight which is evident from the change in viscosity as presented in Table 2.8 Similar observations are reported by A. Hebeish et al.[28] and Mao et al. [83].

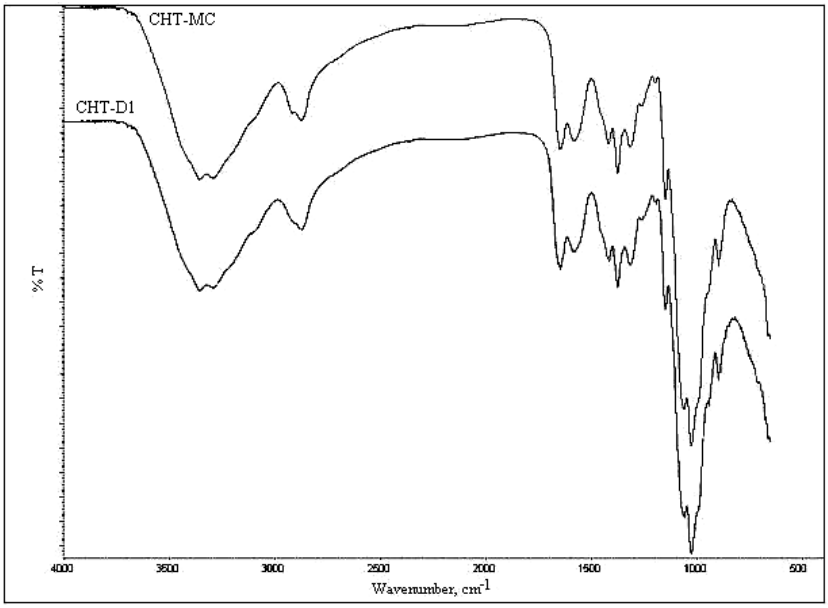


Figure 2.6 FTIR spectra of CHT-MC and its low molecular weight derivative

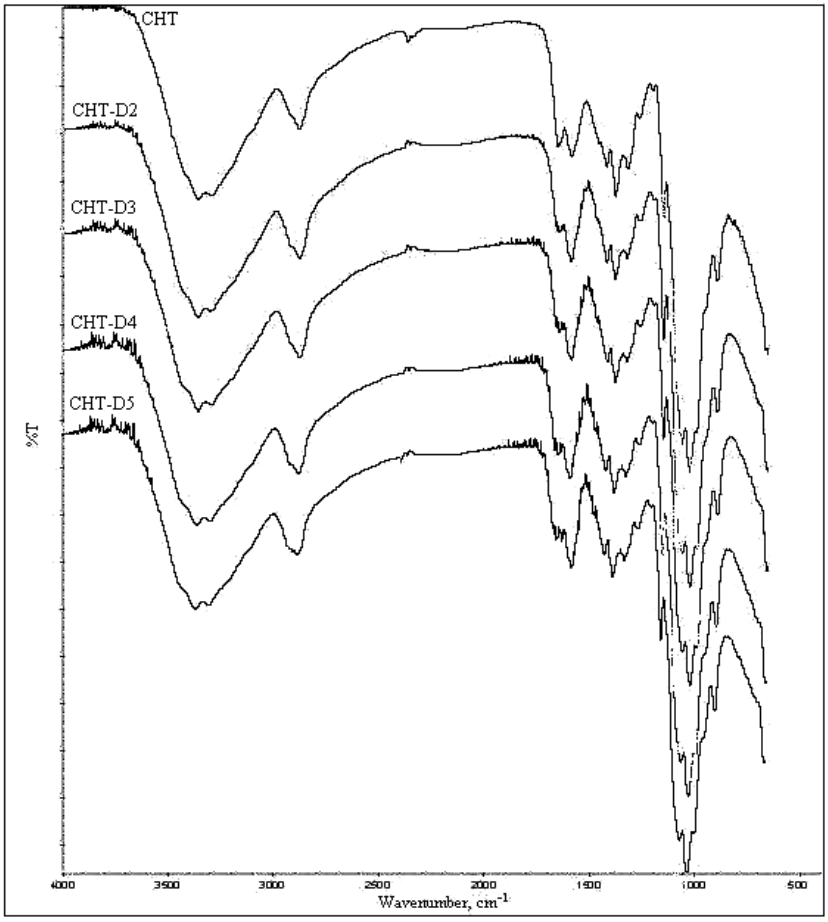


Figure 2.7 FTIR spectra of CHT and its low molecular weight derivatives

2.3.6 Effect of molecular weight and concentration on viscosity of chitosan solutions

It can be seen from Figure 2.5 that the curves of high molecular weight chitosan, namely CHT-MC, CHT and CHT-D1, do not strictly follow the linearity of the Huggins equation (2.6) in the selected range of concentration. These curves show the inflection at a certain critical concentration (C*) and then after the curves bend upwards. Further, the value of C* increases with decrease in molecular weight and ultimately the curves flatten for low molecular weight chitosan, used in this research work. This can be explained on the fact that, when chitosan or any other polymer is added into a solvent, the solvent gradually diffuse into the polymer aggregates resulting into the swelling of the polymer. As swelling continues, the segments of polymer are solvated and loosened out. Since the molecules in a solid polymer are entangled with neighbouring ones, polymer molecules during dissolution diffuse out as bunches of entangled molecules. Even though all chain segments of a polymer molecule in solution are unfolded and fully solvated, the molecules does not assume the shape of an extended straight chain but present in a coil form. These coils or aggregates offer resistance for the mobility or flow of molecules and hence impart viscosity [67, 84]. When the molecular size and concentration are increased, as in this case, the extent of entanglement is increased as shown in Figure 2.8.

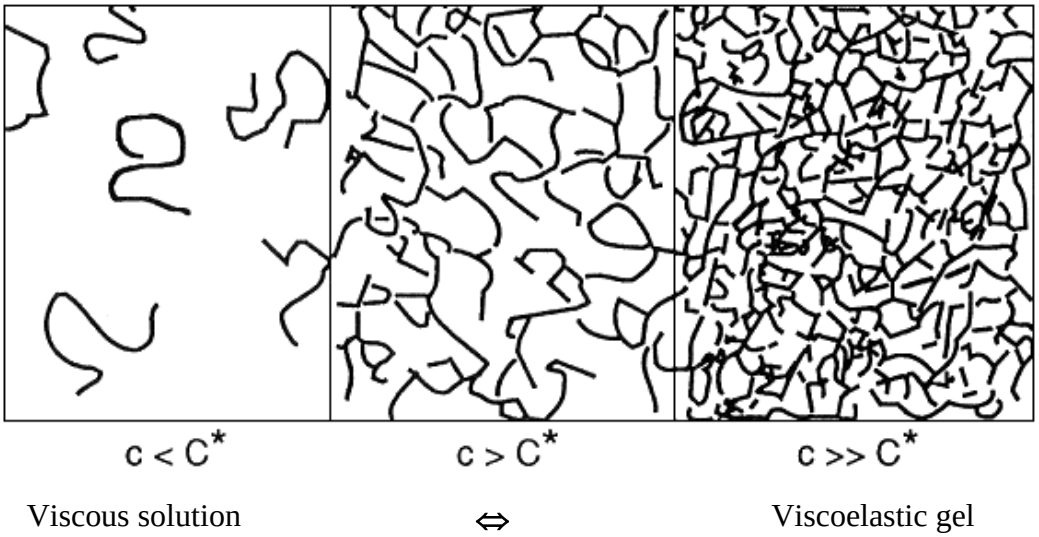


Figure 2.8 Aggregation of chitosan molecules as a function of molecular weight and concentration

In other words the critical concentration (C*) is, indeed, the 'overlap' concentration. Thus, when C>C* the intermolecular entanglements or aggregation predominate and precludes the overall molecular motion of polymers, while individual polymer molecules are statistically separated from other molecules at C<C*. Thus, the critical concentration (C*) is a measure of molecular size and conformation of a polymer, the higher the molecular weight and the more rigid conformation, the lower will be the C*. The results are in close agreement with earlier reports [85, 86]. Hence low molecular weight chitosans can be conveniently used for textile application and applied at reasonably higher concentrations.

2.3.7 Effect of storage time on viscosity of chitosan solution

Polymeric chemicals are generally applied to textiles by padding technique where it is required to prepare a standing bath. Thus the chemical remains in contact with water for a longer period. As biodegradability of chitosan is a well-known phenomenon the effect of storage time on the stability of its solution was studied in terms of change in solution viscosity. The molecular weight of CHT-MC is extremely high for textile applications and synthesis of various derivatives due its very high viscosity. Hence the chitosan having moderate viscosity and molecular weight, namely CHT, was chosen for most of studies hereafter. The stability behaviour of CHT solution in terms of viscosity behaviour and molecular weight determination as a function of storage time presented in Table 2.9 and Table 2.10 and Figure 2.9. The intrinsic viscosity of CHT solutions at different storage times was obtained from Figure 2.9. The molecular weights of CHT were determined by substituting intrinsic viscosities values in Mark-Houwink equation (2.5), which are presented in Table 2.11 and graphically in Figure 2.10.

Table 2.9 Effect of storage time on viscosity of CHT solution

Conc (C), g/dL	Flow time (T, Sec) at storage time (h):					
	0	**24**	**72**	**120**	**192**	**264**
0.1	21.27	20.39	19.92	19.77	-	-
0.2	28.27	26.69	25.23	24.69	24.25	23.65
0.3	37.23	35.02	31.79	31.20	-	-
0.4	49.14	44.40	40.16	38.28	36.95	35.29
0.5	62.61	56.81	50.45	46.98	-	-
0.6	78.69	70.03	60.95	56.53	53.58	50.05
0.7	98.32	86.14	74.45	68.64	-	-
0.8	125.28	105.49	91.14	81.38	74.02	69.83
0.9	157.41	128.8	108.97	96.43	-	-
1.0	196.00	155.2	130.13	114.58	100.14	91.57

Solvent ingredients: Acetic acid 0.25M, sodium acetate 0.25M, T_0= 15.87 sec

Table 2.10 Reduced viscosity of CHT solution as a function of storage time

Conc (C), g/dL	Reduced Viscosity ($\eta_{red} = \eta_{Sp}/C$)at storage time (h):					
	0	**24**	**72**	**120**	**192**	**264**
0.1	3.4	2.85	2.55	2.46	-	-
0.2	3.91	3.41	2.96	2.78	2.64	2.45
0.3	4.49	4.02	3.34	3.22	-	-
0.4	5.24	4.50	3.83	3.53	3.32	3.06
0.5	5.89	5.16	4.36	3.92	-	-
0.6	6.60	5.69	4.73	4.27	3.96	3.59
0.7	7.42	6.33	5.27	4.75	-	-
0.8	8.62	7.06	5.93	5.16	4.58	4.25
0.9	9.91	7.91	6.52	5.67	-	-
1.0	11.35	8.78	7.20	6.22	5.31	4.77

Solvent ingredients: Acetic acid 0.25M, sodium acetate 0.25M, T_0= 15.87 sec

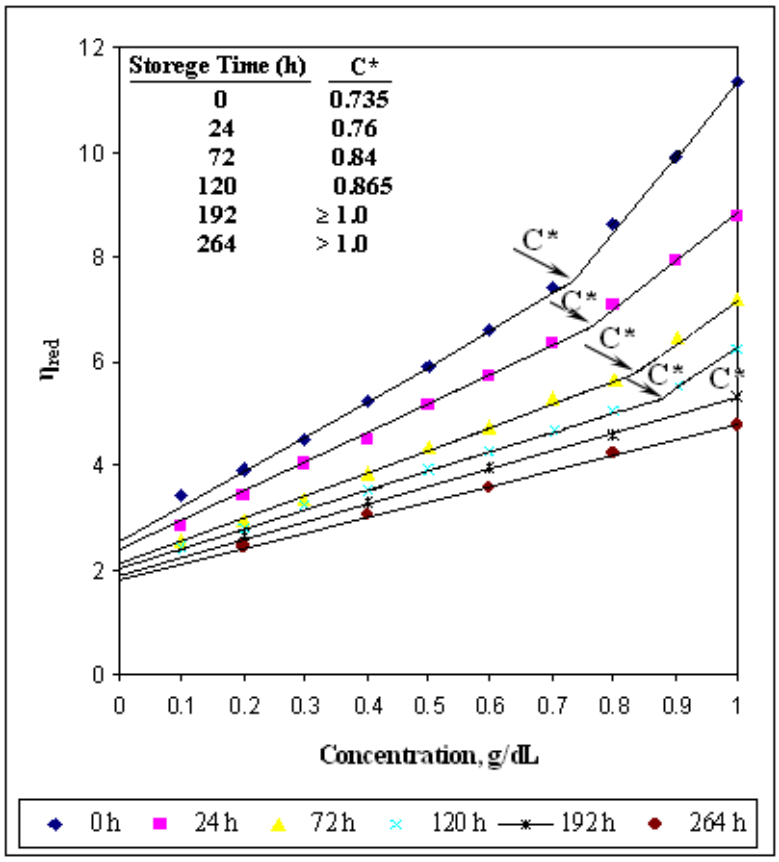


Figure 2.9 Viscosity of chitosan (CHT) solution as a function of storage time

Table 2.11 Effect of storage time on stability chitosan (CHT) solution

Storage time, h	Intrinsic viscosity [η]	Molecular weight (Mv)	Critical concentration (C*), g/dL
0	2.55	135,839	0.735
24	2.2	113,704	0.76
72	2.1	107,506	0.84
120	2.05	104,430	0.865
192	1.95	98,323	≥ 1.0
264	1.9	95,294	>1.0

Solvent: Acetic acid 0.25M, sodium acetate 0.25M, T_0= 15.87 sec

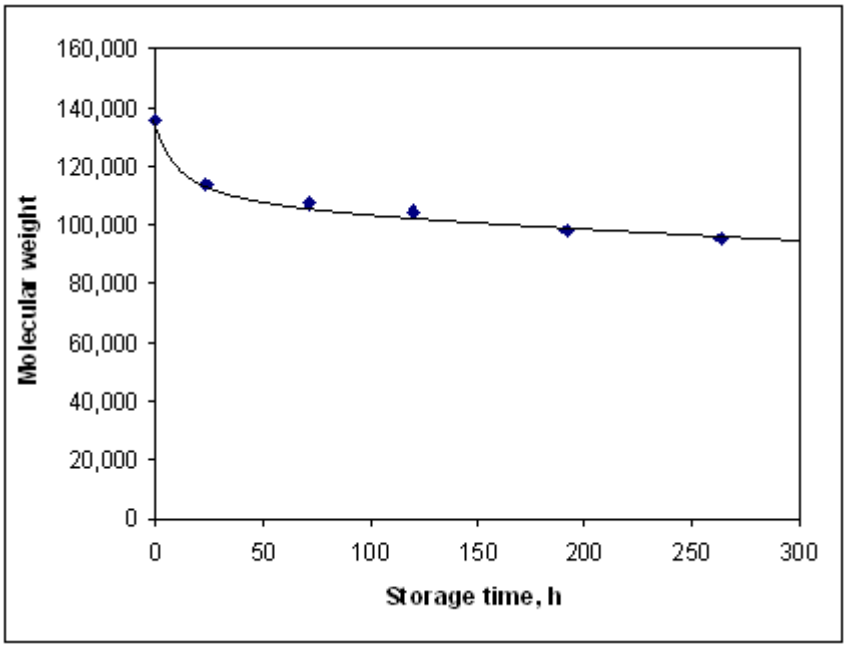


Figure 2.10 Effect of storage time of chitosan (CHT) solution on molecular weight

It is seen from Table 2.11, Figure 2.9 and Table 2.12 that the initial molecular weight and the concentration of polymer have the influence on the stability of the solution. The reduced viscosity curve is observed to be segmented with an overlap/ critical concentration (C*) at the point of inflection and then flattened as the storage time was increased i.e. the critical concentration shifted towards right. It is also observed from Figure 2.10 that the drop in viscosity in first 24 h was much faster and was more significant at higher concentration i.e. above C* as illustrated in Table 2.11. The loss in viscosity may be attributed to the biodegradation of chitosan molecules and/or hydrolysis of polymer molecules and slow detachment of polymer segments from the entanglements which are present above C*. Initially the large molecules, especially at higher concentration, occupy large "hydrodynamic" volume due to aggregation as result of intermolecular cross linkages, which leads to less mobility indicating higher viscosity. The hydrolytic degradation of the polymer leads to the production of smaller molecular entities which in turn causes a drop in hydrodynamic volume of the polymer molecules resulting in higher molecular mobility and as a result reduces the viscosity of the solution [57, 84, 86]. It shows that dilute chitosan solutions made from low molecular weight samples (e.g. CHT-D5) are more stable in terms of viscosity behaviour as illustrated in

Table 2.13, Figure 2.11 and Table 2.14. Hence lower molecular weight chitosan solutions particularly at low concentration may be preferred for textile applications as their standing baths have more consistent viscosity.

Table 2.12 Effect of initial concentration on stability of chitosan (CHT) solution

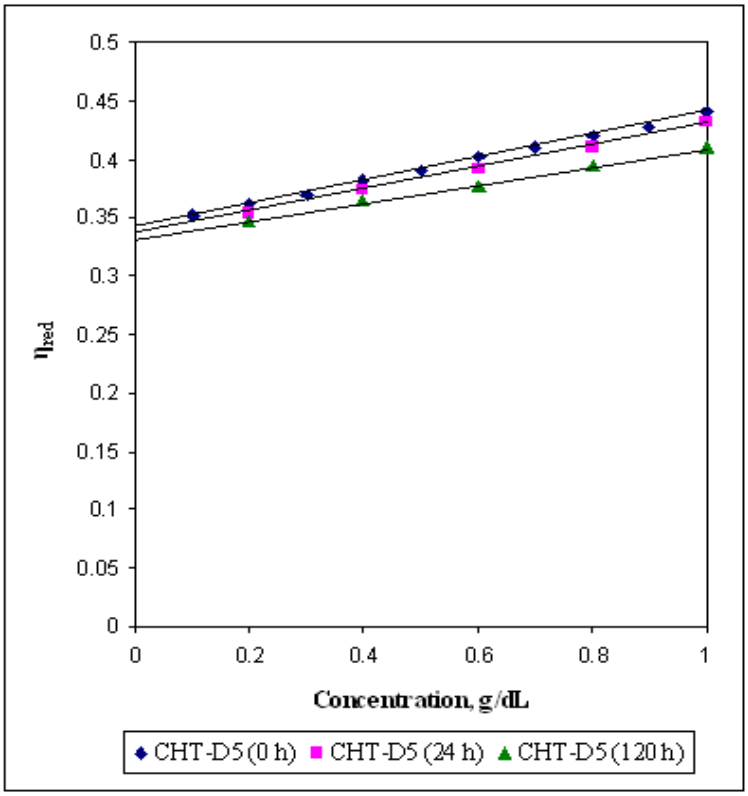
Storage time, h	Change in viscosity (%) of CHT from initial solution at concentrations:	
	0.2 g/dL	1.0 g/dL
0	100	100
24	87.22	77.36
72	75.70	63.43
120	71.10	54.80
192	67.52	46.78
264	62.66	42.03

Solvent: Acetic acid 0.25M, sodium acetate 0.25M, T_0= 15.87 sec

Table 2.13 Effect of storage time on viscosity of low molecular weight chitosan, CHT-D5 solution

Conc (C), g/dL	Viscosity of CHT-D5 solution at storage time:					
	0 h		24 h		120 h	
	Flow time (T), sec	Reduced viscosity (η_{red})	Flow time (T), sec	Reduced viscosity (η_{red})	Flow time(T), sec	Reduced viscosity (η_{red})
0.1	16.43	0.35	-	-	-	-
0.2	17.02	0.36	16.99	0.35	16.97	0.35
0.3	17.63	0.37	-	-	-	-
0.4	18.30	0.38	18.24	0.37	18.18	0.36
0.5	18.96	0.39	-	-	-	-
0.6	19.70	0.40	19.60	0.39	19.47	0.38
0.7	20.44	0.41	-	-	-	-
0.8	21.20	0.42	19.77	0.41	20.88	0.39
0.9	22.00	0.43	-	-	-	-
1.0	22.87	0.44	22.74	0.43	22.39	0.41

Solvent ingredients: Acetic acid 0.25M, sodium acetate 0.25; T_0 15.87 sec



CHT-D5: Mol wt 11,986

Figure 2.11 Viscosity of CHT-D5 solution as a function of storage time

Table 2.14 Effect of storage time on stability chitosan (CHT-D5) solution

Storage time, h	Intrinsic viscosity [η]	Molecular weight (Mv)
0	0.34	11,986
24	0.334	11733
120	0.33	11564

Solvent ingredients: acetic acid 0.25M, sodium acetate 0.25M, T_0 15.87 sec

2.3.8 Effect of electrolyte on viscosity of chitosan solution

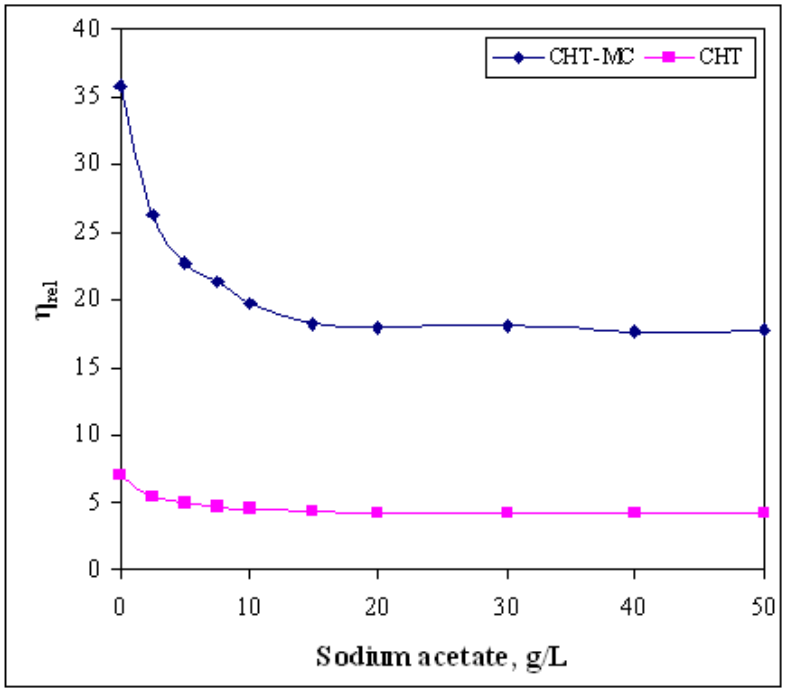
Chitosan, being a polycationic material having pKa value 6.3, requires acidic pH is for its dissolution [69]. The conformational arrangements of polyelectrolyte chains, mainly responsible for viscosity behaviour, are influenced by various factors such as pH, concentration of polyelectrolyte, molecular weight, nature of counter ion and added electrolyte etc [87-89]. Chitosan salts such as acetate, formate, lactate, citrate, chloride, and nitrate are soluble in water [69] while sulphate salt is insoluble [90, 91]. The effect of

pH on chitosan chain conformational arrangements in aqueous medium can be understood due to the protonation of amino groups, which is responsible for the charge extension on the polyelectrolyte chains [87]. Polyanions such as sodium tripolyphosphate (TPP) lead to ionotropic gelation of chitosan, which is one of the fundamental principles of nano chitosan synthesis [92]. Velásquez et al [93] reported the effect of sodium chloride on the behaviour of two chitosan salts namely nitrate and chloride. The η_{red} values for chitosan nitrate were found to be markedly more affected than chitosan chloride by the increasing added ionic strength of the medium. According to them, nitrate counter ions cause a lesser stiffness than chloride counter ions, which has been attributed to higher screening due to bigger nitrate ions. The application of chitosan for the syntheses of various derivatives and in textiles, in this research, was mainly employed in acetic acid solution with sodium acetate as electrolyte. Therefore, the effect of sodium acetate concentrations on two different grades of chitosan namely, CHT-MC and CHT was studied as demonstrated in Table 2.15 and graphically in Figure 2.12.

Table 2.15 Effect of sodium acetate concentration on viscosity of chitosan solutions

Sod. Acetate Concentration, g/L	**T_0, sec**	**CHT-MC solution**		**CHT solution**	
		Flow time (T), sec	**Relative viscosity (η_{rel})**	**Flow time (T), sec**	**Relative viscosity (η_{rel})**
0	15.58	557.8	35.8	110.68	7.1
2.5	15.60	409.2	26.2	82.79	5.3
5	15.63	354.47	22.7	77.91	5.0
7.5	15.68	332.71	21.2	73.52	4.7
10	15.71	310.35	19.8	71.32	4.5
15	15.78	285.63	18.1	67.92	4.3
20	15.82	282.72	17.9	67.61	4.3
30	15.85	284.75	17.9	67.60	4.3
40	16.23	286.70	17.7	67.81	4.2
50	16.37	289.63	17.6	68.03	4.2

Chitosan 5 g/L, acetic acid 15 g/L, flow time for water = 15.57 sec at 30 ^{0}C,
T_0 represents blank reading for solution containing acetic acid 15 g/L and sodium acetate



Chitosan 5 g/L, Acetic acid 15 g/L, Mol wt: CHT-MC 654,127; CHT 135,869

Figure 2.12 Relative viscosity of chitosan solution as a function of sodium acetate concentration

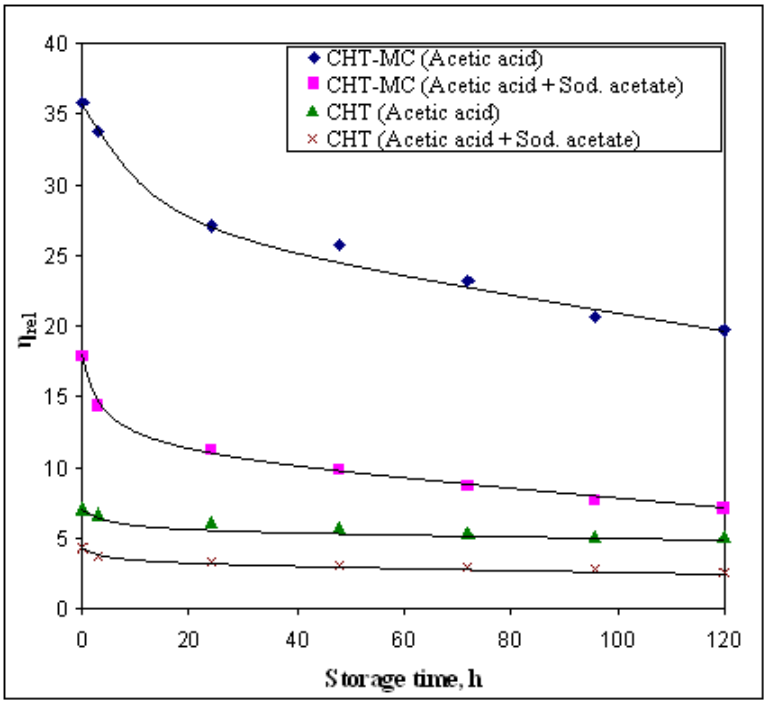
Sodium acetate was found to reduce the viscosity of chitosan solution (Figure 2.12). It was observed that with increase in concentration of sodium acetate, the viscosity of chitosan solution, for a selected concentration of 5 g/L, decreased up to certain concentration (~15g/L). No reduction in viscosity was noticed beyond this concentration. The effect of electrolyte was also observed to be more pronounced on high molecular weight chitosan, CHT-MC. With decrease in molecular weight of chitosan, the amount of sodium acetate required to attain the lower viscosity was decreased i.e. about 7.5 g/L of sodium acetate was required for CHT solution. The decrease in viscosity with increase in electrolyte concentration can be attributed to the shielding effect of counter ions [69]. Due to ion dipole forces; the acetate ions form a cascade negative charge over each chitosan molecule establishing repulsive forces between them. This offers low resistance to the flow or mobility of polymer molecules. As the number of amino groups content is large in high molecular weight chitosan, higher charge screening is effected due to added electrolytes resulting in to intensive lowering in viscosity of the solution [93]. The drop in viscosity of chitosan solution due to sodium acetate was found to be almost uniform

during storage period as shown in Table 2.16 and graphically in Figure 2.13. The stability of chitosan solution, thus, is influenced by storage time and the presence of electrolyte. Thus almost a stable chitosan solution can be obtained by the judicious selection of low molecular weight chitosan and optimum concentration of electrolyte.

Table 2.16 Effect of sodium acetate on storage stability of chitosan solution

Storage time, h	CHT-MC				CHT			
	Flow time (T), Sec		Relative viscosity (η_{rel})		Flow time (T), Sec		Relative viscosity (η_{rel})	
	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
0	557.8	282.7	35.80	17.87	110.7	67.6	7.11	4.27
3	526.3	227.3	33.78	14.37	104.0	59.5	6.68	3.76
24	422.7	178.6	27.13	11.29	96.1	53.8	6.17	3.40
48	402.1	155.2	25.81	9.81	89.0	48.5	5.71	3.07
72	362.5	137.5	23.27	8.69	84.0	46.1	5.39	2.91
96	321.4	121.1	20.63	7.65	80.2	43.8	5.15	2.77
120	307.5	112.3	19.74	7.10	78.5	41.2	5.04	2.60

Chitosan 5 g/L, (A) Solvent: Acetic acid 15 g/L, T_0 15.58 sec at 30 ^{0}C;
(B) Solvent: Acetic acid 15 g/L + Sodium acetate 20 g/L, T_0 15.82sec at 30 ^{0}C



Chitosan 5 g/L, Acetic acid 15 g/L, Sodium acetate 20 g/L

Figure 2.13 Effect of sodium acetate on storage stability of chitosan solution

2.3.9 Application of chitosan (CHT) derivatives on cotton fabric: Pad-Dry-Cure process

Chitosan can be applied to cotton fabric by exhaustion method or by padding method. The viscous nature of chitosan solution, however, restricts its application by exhaust method due the possibility of uneven sorption. The second method, which is prevalent in continuous dyeing or finishing processes of textiles, produces uniform effects and is most suitable for polymeric applications. Hence, the pad-dry cure method for the treatment of cotton fabric with different molecular weight chitosan derivatives (Table 2.8) was adopted. Since the treated fabric samples, in many cases, had to evaluate with optical instruments (CCMS), any changes in fabric construction due to above treatments could lead to variations in results. In order to minimize the error, fabric sample was padded with a solution containing acetic acid (15 ml/L) and sodium acetate (10 g/L), this sample was termed as 'control'.

Table 2.17 Effect of various treatments on fabric construction

Fabric Sample	Treatment	Ends/in (EPI)	Picks/in (PPI)
Untreated	-	142.0	72.0
Control	Blank treated*, (Pad-Dry cure)	149.1	76.4
CHT-MC	10 gpl (Pad-Dry cure)	149.4	75.9
CHT-D1	10 gpl (Pad-Dry cure)	148.6	76.1
CHT	10 gpl (Pad-Dry cure)	148.1	77.1
CHT-D2	10 gpl (Pad-Dry cure)	148.8	76.4
CHT-D3	10 gpl (Pad-Dry cure)	149.0	77.2
CHT-D4	10 gpl (Pad-Dry cure)	148.4	75.6
CHT-D5	10 gpl (Pad-Dry cure)	150.0	76.4

**Blank treatment: Acetic acid 15 ml/L, sodium acetate 10 g/L*

The fabric construction in terms of ends/in (EPI) and picks/in (PPI) (average of five readings) measured at different stages of treatment is presented in Table 2.17. It was observed that the fabric construction was not much affected due to such treatments and was very much close to the 'control' sample. Therefore the computer colour matching system was safely employed for the evaluation of appearance (indices) and colour (K/S values).

2.3.10 Surface morphology of chitosan treated fibres

Chitosan solutions (1 g/L) were applied on cotton fabric by conventional pad-dry cure technique and the surface morphology of the treated and untreated cotton was studied under scanning electron microscope, which is presented in Figure 2.14. Chitosan exhibits an inherent film formation property, which is clearly seen as gloss on fibre surface as shown in Figure 2.14 (b & c). Further the film deposition on fibre surface can be confirmed by prolong boiling of treated sample in distilled water so that the broken appearance of film can be viewed under SEM, as presented in Figure 2.14 (d). The molecular weight of the treated chitosan seems to play some role on the surface appearance in micrograph, the higher gloss of notices in higher molecular weight chitosan (CHT-MC) treated fibres. The micrograph of low molecular weight chitosan (CHT-D4) treated cotton fibres however looks somewhat different with slightly non glossy surface [Figure (e & f)] indicating the penetration of polymeric material in to the fibre structure. This may be attributed to the lower viscosity of low molecular weight chitosans that facilitates better penetration and high molecular weight chitosan having high viscosity confined to the surface depositions only.

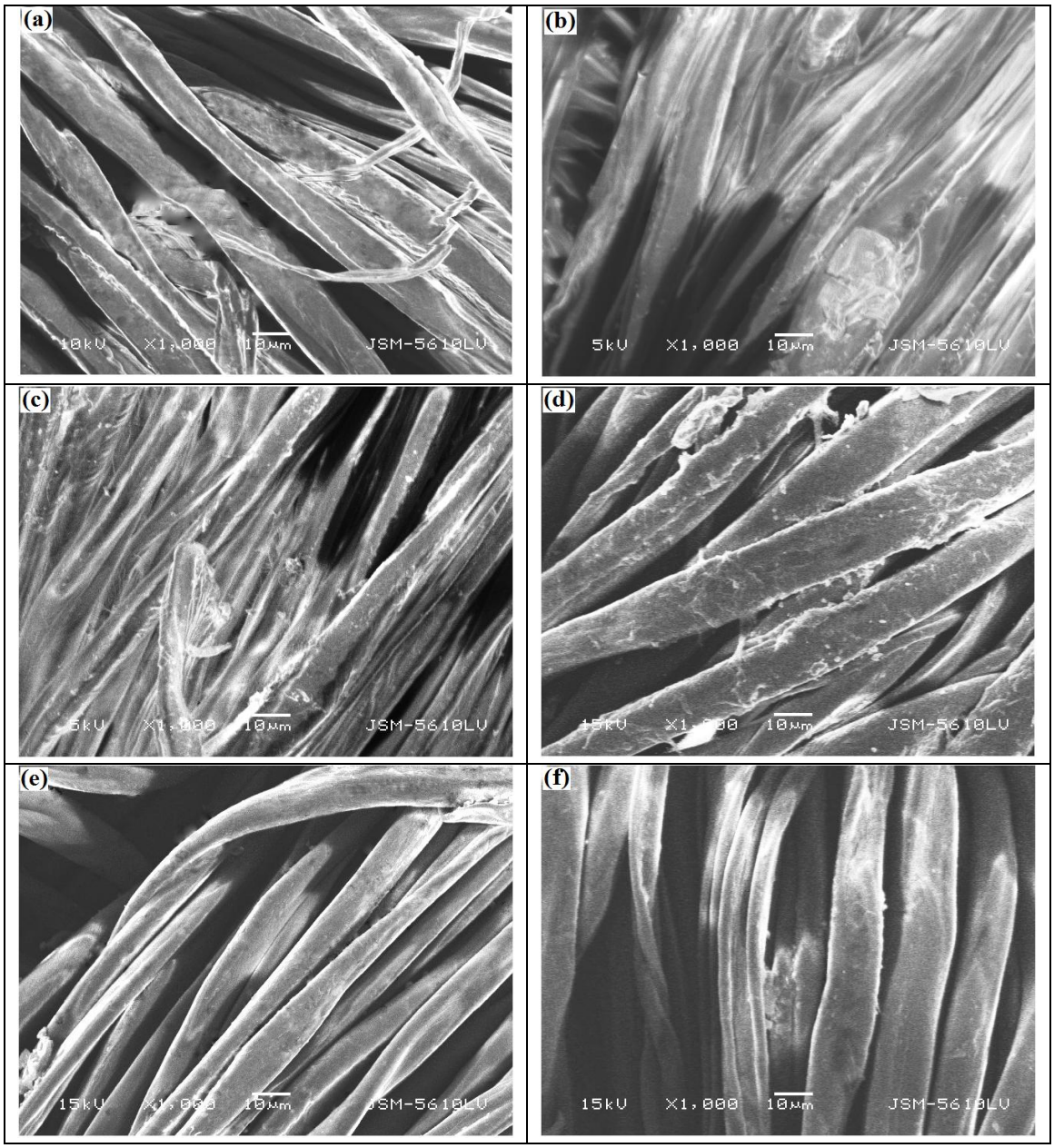


Figure 2.14 Scanning electron microphotographs (x1000) of (a) Cotton Fibre (control), (b) CHT-MC treated fibres, (c) CHT treated fibres (d) CHT treated and then prolong boiled cotton fibres, (e) CHT-D4 treated fibres and (f) CHT-D5 treated fibres

2.3.11 Effect of chitosan treatment on appearance and feel of cotton fabric

The appeal of the fabric is manifested by its appearance and the feel. Various factors such as colour and transparency of the polymeric film (chitosan), presence of functional groups, penetration level of chitosan into fibre/fabric structure etc influence

the appearance of treated cotton fabric. Level of deposition of polymer film on fibrous material is determined by the viscosity of its solution (padding liquor) which in turn is determined by its molecular weight and concentration in pad liquor [67, 68]. These two factors also influence the feel of the treated fabric. In order to understand the influence of chitosan treatment on cotton fabric, the appearance was evaluated in terms of whiteness index (W.I.), yellowness index (Y.I.) and brightness index (B.I.); and the feel in terms of stiffness (measured in bending length with the average of four readings) of different molecular weight chitosans at different concentrations. Results of these properties are presented in Tables 2.18 (A & B) & Tables 2.19(A & B) respectively and graphically in corresponding Figures 2.15, 2.16, 2.17 and 2.18.

Table 2.18A Appearance of chitosan treated cotton fabric as a function of molecular weight and concentration

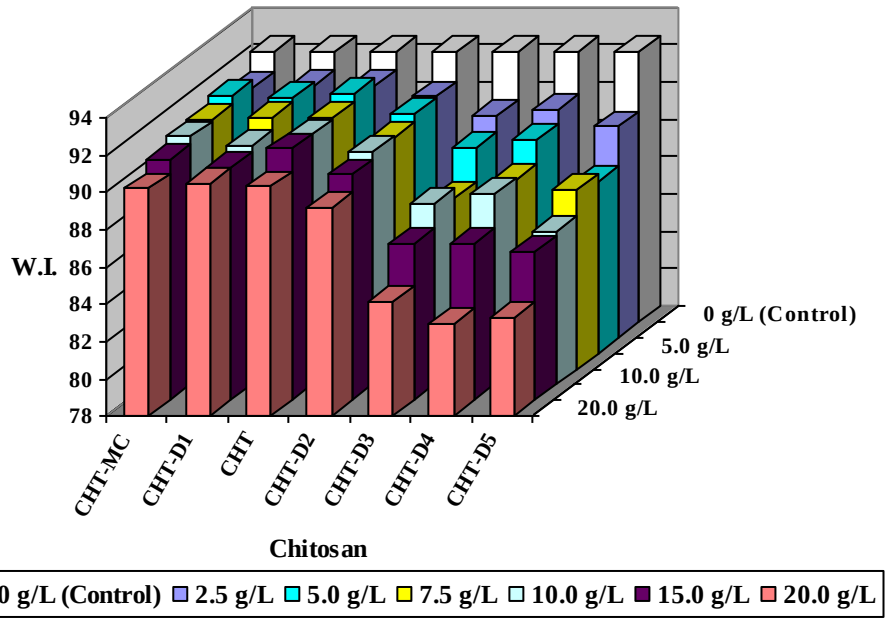
Conc, g/L	CHT-MC (654,127)			CHT-D1 (285,231)			CHT (135,839)			CHT-D2 (71,676)		
	WI	YI	BI	WI	YI	BI	WI	YI	BI	WI	YI	BI
2.5	91.4	3.6	82.4	91.5	3.7	82.3	91.5	3.3	81.6	90.9	3.6	81.4
5.0	91.8	3.6	83.2	91.7	3.6	82.6	91.9	3.4	81.4	90.8	3.6	81.6
7.5	91.4	4.7	82.2	91.5	4.3	81.8	91.5	4.3	80.6	90.4	4.0	82.9
10.0	91.3	4.4	81.9	90.8	4.3	81.6	91.4	4.7	80.6	90.5	4.3	82.6
15.0	90.9	4.9	81.3	90.5	4.8	80.5	91.5	4.5	79.8	90.1	4.7	82.3
20.0	90.2	5.4	79.8	90.5	5.6	80.1	90.3	5.4	77.9	89.2	5.8	79.9

Values in parentheses indicate the mol wt of chitosan,
Indices of control sample: WI= 92.5, YI= 2.6, BI= 84.6

Table 2.18B Appearance of chitosan treated cotton fabric as a function of molecular weight and concentration

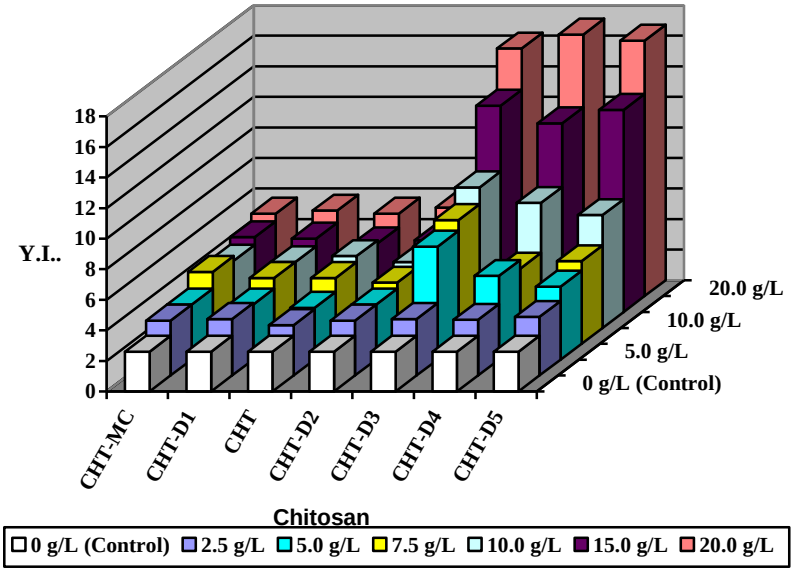
Conc, g/L	CHT-D3 (38,733)			CHT-D4 (20,698)			CHT-D5 (11,986)		
	WI	YI	BI	WI	YI	BI	WI	YI	BI
2.5	89.9	3.7	79.8	90.2	3.6	78.9	89.3	3.8	78.1
5.0	89.0	7.4	76.9	89.4	5.5	77.9	87.2	4.8	77.7
7.5	89.2	8.1	76.9	88.1	4.9	75.3	87.6	5.4	74.8
10.0	87.7	9.2	74.2	88.2	8.2	74.8	86.2	7.4	73.1
15.0	86.4	13.5	70.6	86.4	12.4	71.5	86.0	13.2	69.4
20.0	84.1	16.2	66.1	83.0	17.1	68.7	83.3	16.7	66.2

Values in parentheses indicate the mol wt of chitosan,
Indices of control sample: WI= 92.5, YI= 2.6, BI= 84.6



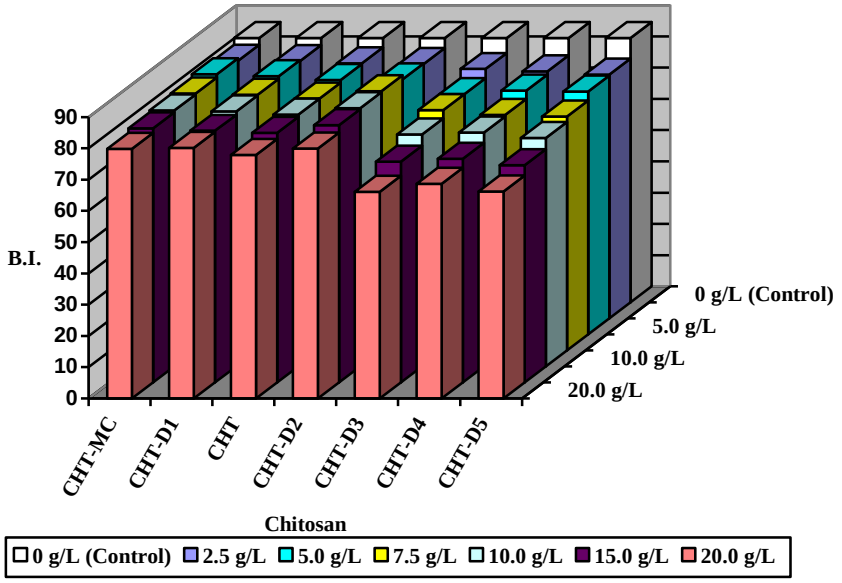
Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.15 Whiteness index (WI) of chitosan treated cotton fabric as a function of molecular weight and concentration



Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.16 Yellowness index (YI) of chitosan treated cotton fabric as a function of molecular weight and concentration



Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.17 Brightness index (BI) of chitosan treated cotton fabric as a function of molecular weight and concentration

The appearance of cotton fabric in terms of reduction in whiteness and brightness indices or rise in yellowness indices was influenced by normal chitosan as shown in Figure 2.15, Figure 2.16 and Figure 2.17. The whiteness and the brightness of parent chitosan i.e. CHT-MC and CHT treated fabrics were found to be satisfactory and were slightly decreased with increase in concentration of chitosan nevertheless they were in tolerable limits. The appearance of depolymerized chitosan treated fabrics, however, was found to be deteriorated more than that of parent chitosan treated fabrics. The whiteness and brightness of depolymerized chitosan treated samples were decreased severely with decrease in molecular weight and increase in concentration. The loss in whiteness or discolouration in depolymerized chitosan treated fabric may be due the possible liberation of nitric oxide gas from $NaNO_2$ in acidic medium that gets adsorbed on various functional groups of chitosan imparting yellowness [94]. The higher extent of (increased) discolouration of treated fabric due to depolymerized chitosan was thus governed by the amount of sodium nitrite used. It seems further that the excessive depolymerisation by sodium nitrite produces undesired impurities containing aldehyde end groups, which may react with free amino groups to form –N=C bond causing yellowness. The reduction in

brightness of depolymerized chitosan treated fabric may be ascribed to the loss in gloss of fibre surface due to morphological changes occurred due to diffusion of oligomer into the fibre structure, which can be observed as matty surface as shown in scanning electron microphotographs in Figure 2.14(d & e).

Table 2.19A Stiffness of chitosan treated fabric as a function of molecular weight and concentration

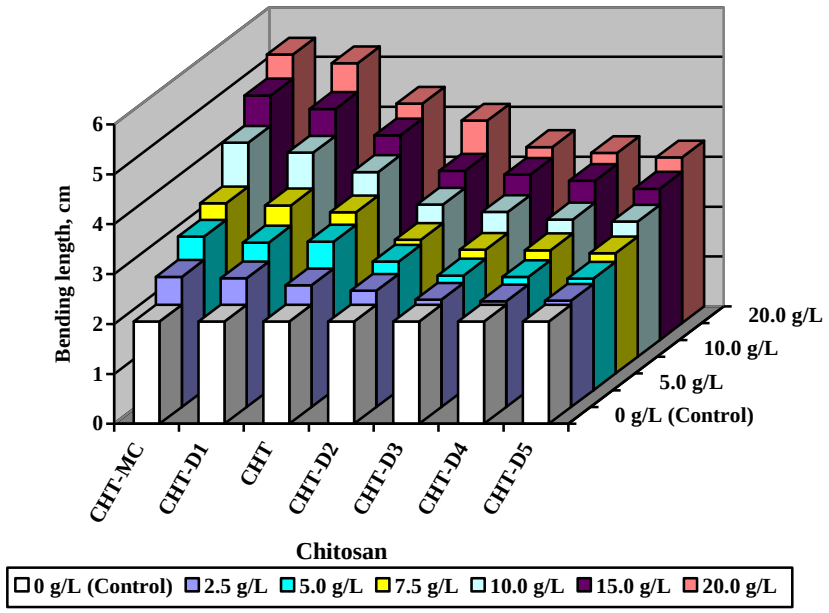
Conc, g/L	Bending length, cm							
	CHT-MC (654,127)		CHT-D1 (285,231)		CHT (135,839)		CHT-D2 (71,676)	
	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
2.5	2.61	1.76	2.58	1.72	2.44	1.70	2.33	1.85
5.0	3.08	2.10	2.96	2.10	2.98	2.05	2.58	1.85
7.5	3.41	2.55	3.37	2.40	3.23	2.25	2.68	2.01
10.0	4.29	3.03	4.09	2.89	3.70	2.74	3.05	2.19
15.0	4.90	3.23	4.63	3.11	4.10	3.00	3.39	2.21
20.0	5.38	3.53	5.21	3.38	4.40	3.33	4.06	2.88

Values in parentheses indicate the mol wt of chitosan,
Bending length of control sample: warp = 2.05 cm and weft = 1.68 cm

Table 2.19B Stiffness of chitosan treated fabric as a function of molecular weight and concentration

Conc, g/L	Bending length, cm					
	CHT-D3 (38,733)		CHT-D4 (20,698)		CHT-D5 (11,986)	
	Warp	Weft	Warp	Weft	Warp	Weft
2.5	2.15	1.70	2.12	1.69	2.13	1.70
5.0	2.30	1.71	2.27	1.68	2.24	1.70
7.5	2.48	1.86	2.47	1.76	2.41	1.73
10.0	2.90	2.00	2.75	1.94	2.71	1.88
15.0	3.31	2.38	3.19	2.21	3.03	1.96
20.0	3.53	2.68	3.41	2.43	3.32	2.11

Values in parentheses indicate the mol wt of chitosan,
Bending length of control sample: warp = 2.05 cm and weft = 1.68 cm



Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.18 Stiffness of chitosan treated cotton fabric as a function of molecular weight and concentration

The handle of the fabric on chitosan treatment was adversely affected as seen from the rise in fabric stiffness with increase in concentration and the molecular weight of chitosan shown in Table 2.19A and Table 2.19B and Figure 2.18. The fabric stiffness and feel treated with low molecular weight chitosan namely CHT-D4 and CHT-D5 were found to be satisfactory and well in acceptable limits. The fabric surface was also found to be excessively harsh in case of high molecular weight chitosan and the inherent appeal of cotton or 'cotton feel' was almost lost. The rigid conformation of chitosan structure and due to the formation of large number of intra and intermolecular cross linkages due to amino and hydroxyl groups as shown in Figure 1.5 (Chapter 1), chitosan produces stiff films [95]. High viscosity solutions of large chitosan molecules confine the rigid film deposition onto fabric surface only thus imparting stiffness to fabric. The presence of chitosan films of high molecular weight chitosans (CHT-MC and CHT) can be clearly seen from Figure 2.14 (b & c). This property is undesired in pretreated fabrics but may be beneficial when applied during finishing process, which impart firmness and body to the fabric. Bhuvana et al.[96], in benefit to the uniform film formation of chitosan on fibre surface, have reported the low frictional values offering itself a better candidate as

stiffening agent. The high viscosity solutions, however, cause difficulties during application in padding mangle.

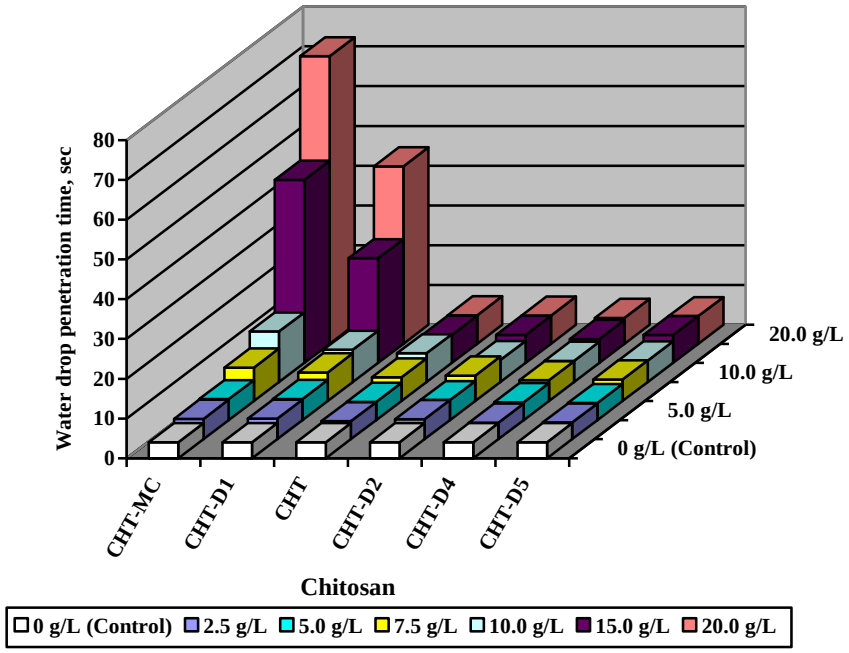
2.3.12 Effect of chitosan treatment on absorbency cotton fabric

Rapid and uniform absorbency for any pretreated fabric is indispensable for the better penetration of dyes and chemicals during the subsequent unit operations like dyeing, printing and finishing. Therefore the effect of chitosan applications on the absorbency was determined, which are shown in Table 2.20 and graphically in Figure 2.19. Absorbency, measured by drop penetration method, reported here are taken as the average of nine readings. The absorbency of chitosan treated fabric was found to be altered by the molecular weight and concentration of applied chitosan. The absorbency of high molecular chitosan (e.g. CHT-MC, CHT-D1 and CHT) treated fabric was high and progressively improved with lowering of molecular weight of chitosan. The absorbency was observed to be reduced with increase in concentration of chitosan. The concentration effect was more substantial in case of high molecular weight chitosan, where as this effect was meager in case of low molecular weight chitosan.

Table 2.20 Absorbency of chitosan treated cotton fabric as a function of molecular weight and concentration

Conc, g/L	Water drop penetration time in seconds treated with:					
	CHT-MC (654,127)	**CHT-D1 (285,231)**	**CHT (135,839)**	**CHT-D2 (71,676)**	**CHT-D4 (20,698)**	**CHT-D5 (11,986)**
2.5	5.1	5.2	4.5	5.0	4.2	4.2
5.0	5.3	5.3	4.6	5.0	4.5	4.3
7.5	8.4	7.2	5.9	6.4	5.3	5.4
10.0	12.7	8.1	7.2	5.5	5.3	5.4
15.0	46.0	26.3	7.1	7.0	6.0	7.0
20.0	72.3	44.6	7.2	7.1	6.5	6.9

Values in parentheses indicate the mol wt of chitosan, Absorbency of control sample: 4.02 sec



Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.19 Absorbency of chitosan treated cotton fabric as a function of molecular weight and concentration

The decreased absorbency in case of high molecular chitosan may be due to the formation of rigid film of chitosan over surface thus acting as a barrier for the penetration of water. The better absorbency conferred by low molecular weight chitosan treatment may be attributed to the capillary action of rough surface formed, which can be clearly visualized from scanning electron microphotographs in Figure 2.14 (d & e). The apparent drop in absorbency of cotton fabric due to chitosan pretreatment, however, is not expected to cause any hindrance on subsequent processing such as dyeing, printing or finishing. Since the poor absorbency of the fabric is due to rigid film formation on surface and not due to the introduction of hydrophobicity. Such chitosan films contain accessible sites such as -OH and $-NH_2$ nevertheless they are heavily crosslinked by hydrogen bonding.

2.3.13 Dyeing behaviour

Textiles made from cotton and other cellulose fibres are conventionally dyed with direct, reactive, azoic, vat, sulphur etc dyes. These dyes are characterized by certain

inherent properties. Vat dye are known for excellent all round fastness properties but have limitations of high price and problems of poor dye bath stability due to susceptibility of leuco vat dye to oxidation. Reactive dyes from covalent linkages/bonding with fibre and confer good fastness to washing. Also, these dyes are available in wide spectrum of colour range. However, their tendencies to readily hydrolyze and moderate fastness to light are the major drawbacks. Azoics produce bright shades but they possess poor rubbing fastness properties. Sulphur dyes are very popular for black and blue colours and some fancy shades such as dull green or olive green, brown etc. The dyeings are fast to washing and light but fastness to bleaching is poor. Direct dyes are known for ease of application and for full colour range availability. These dyes possess strong affinity for cellulosic fibres and therefore, also known as substantive dyes. These dyes, however, suffer from poor fastness to washing and other agencies. Any modifications in fibre, dye bath additives, dyeing process and/or after treatments, direct dyes respond greatly in its behaviour [97, 98]. Under this background direct dyes were selected for studying the dyeing behaviour of chitosan treated cotton in the present research project.

Secondly, the structure of chitosan is very much analogous to cellulose (except that the –OH group in cellulose at C2 is being replaced by $–NH_2$ in chitosan), it is anticipated that its treatment should influence the cellulose dyeing in complimentary. In this work, therefore, the effect of pretreatment and after treatment of chitosan on direct dyeing of cotton and the washing fastness properties of these dyed samples was studied. Accordingly, two direct dyes namely C. I. Direct Red 81 (Mol wt 675.6) and C. I. Direct Blue 71 (Mol wt 1029.9) shown in Table 2.1 were selected. Attributing to the presence of cationic amino groups, the effect of chitosan pre- treatment on the dyeability towards acid dyes (C. I. Acid Blue 158, Table 2.1) was also investigated.

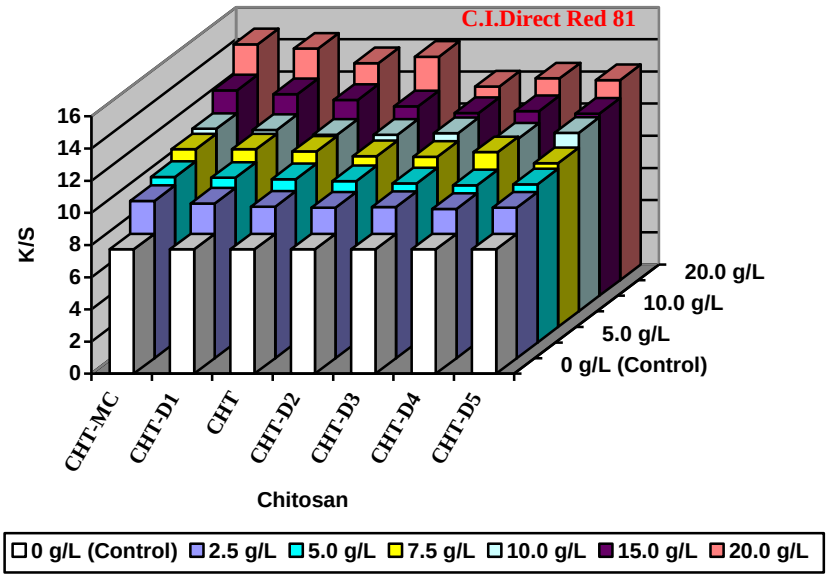
2.3.13.1 Effect of chitosan pretreatment on direct dyeing of cotton fabric

The chitosan, of varying degree of molecular weight, pretreated at different concentrations by pad-dry cure method was dyed with direct dyes mentioned above. The dye uptake, measured in terms of K/S, by these samples is presented in Table 2.21 and Table 2.22; and fastness properties in Table 2.24 and Table 2.25.

Table 2.21 C. I. Direct Red 81 uptake of chitosan treated cotton fabric as a function of molecular weight and concentration

Conc, g/L	K/S values of C. I. Direct Red 81 dyed samples pretreated with:						
	CHT-MC (654,127)	**CHT-D1 (285,231)**	**CHT (135,839)**	**CHT-D2 (71,676)**	**CHT-D3 (38,733)**	**CHT-D4 (20,698)**	**CHT-D5 (11,986)**
2.5	9.77 *[26]*	9.61 *[24]*	9.41 *[22]*	9.35 *[21]*	9.39 *[22]*	9.28 *[20]*	9.36 *[21]*
5.0	10.29 *[33]*	10.24 *[32]*	10.16 *[32]*	10.03 *[30]*	9.90 *[28]*	9.77 *[26]*	9.84 *[27]*
7.5	11.04 *[43]*	11.04 *[43]*	10.90 *[41]*	10.61 *[37]*	10.57 *[37]*	10.86 *[40]*	10.48 *[36]*
10.0	11.34 *[47]*	11.28 *[46]*	10.97 *[42]*	10.98 *[42]*	11.08 *[43]*	10.74 *[39]*	11.09 *[43]*
15.0	12.77 *[65]*	12.53 *[62]*	12.17 *[57]*	11.78 *[52]*	11.36 *[47]*	11.48 *[49]*	11.31 *[46]*
20.0	14.65 *[90]*	14.39 *[89]*	13.48 *[74]*	13.89 *[80]*	12.04 *[56]*	12.54 *[62]*	12.43 *[60]*

Values in parentheses indicate the mol wt of chitosan, Dye: 1% o.w.m.; K/S value of control sample is 7.73; Values in brackets indicate the per cent improvement in colour value compared to control sample



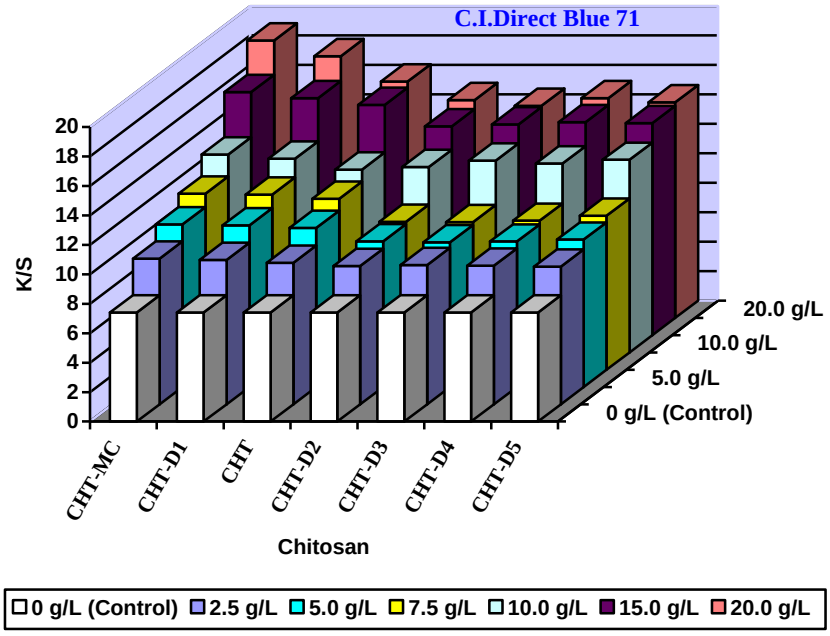
Dye: 1% o.w.m, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.20 C. I. Direct Red 81 uptake of chitosan treated cotton fabric as a function of molecular weight and concentration

Table 2.22 C. I. Direct Blue 71 uptake of chitosan treated cotton fabric as a function of molecular weight and concentration

Conc, g/L	K/S values of C.I. Direct Blue 71 dyed samples pretreated with:						
	CHT-MC (654,127)	CHT-D1 (285,231)	CHT (135,839)	CHT-D2 (71,676)	CHT-D3 (38,733)	CHT-D4 (20,698)	CHT-D5 (11,986)
2.5	9.89 *[33]*	9.81 *[32]*	9.60 *[30]*	9.39 *[27]*	9.46 *[28]*	9.41 *[27]*	9.34 *[26]*
5.0	11.04 *[49]*	10.98 *[48]*	10.81 *[46]*	9.90 *[33]*	9.82 *[33]*	9.88 *[33]*	10.01 *[35]*
7.5	11.96 *[61]*	11.90 *[61]*	11.60 *[57]*	10.05 *[36]*	10.02 *[35]*	10.12 *[37]*	10.45 *[41]*
10.0	13.44 *[81]*	13.16 *[78]*	12.42 *[68]*	12.58 *[70]*	13.03 *[76]*	12.82 *[73]*	13.08 *[77]*
15.0	16.50 *[123]*	16.09 *[117]*	15.64 *[111]*	14.18 *[91]*	14.32 *[93]*	14.47 *[95]*	14.39 *[94]*
20.0	18.83 *[154]*	17.76 *[140]*	16.05 *[117]*	14.79 *[99]*	14.40 *[94]*	14.92 *[101]*	14.63 *[97]*

Values in parentheses indicate the mol wt of chitosan, Dye: 1% o.w.m, K/S value of control sample is 7.41, Values in brackets indicate the per cent improvement in colour value compared to control sample



Dye 1% o.w.m, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.21 C. I. Direct Blue 71 uptake of chitosan pretreated cotton fabric as a function of molecular weight and concentration

The dye uptake (K/S values) for C. I. Direct Red 81 and C. I. Direct Blue 71 by chitosan treated cotton fabric was improved substantially as observed from Table 2.21 and Table 2.22 (Figure 2.20 and Figure 2.21). The uptake was increased with the increase in the concentration of chitosan for a particular molecular weight grade and also the same was increased with increase in molecular weight for varying molecular weight chitosan treatment especially at higher concentration. The dye uptake of low molecular weight chitosan treated samples from CHT-D2 to CHT-D5 was almost remained unchanged for a particular concentration. The dyeing behaviour of chitosan treated fabric, however, was somewhat different for two dyes selected for the experiment. Blue dye showed high substantivity towards chitosan treated fabric than the red.

The enhanced dye uptake due to chitosan may be attributed to the cationic amino groups forming dye sites, which interact with direct dye through hydrogen bonding as well as ionic linkages. High molecular weight chitosan, due to highly viscous nature of their solutions, are confined mostly on the fibre surface resulting greater accumulation of dye on the surface. Also, the number of amino groups is increased with increase in molecular weight and with increase in concentration. It can be observed from the structures of C. I. Direct Red 81 and C. I. Direct Blue 71 (Table 2.1) that the molecular weight of blue dye is high and is characterized by greater degree of planarity due to conjugation system possessing high substantivity and moderate to good wet fastness properties. The structure also shows four anionic ($-SO_3^-$) groups that can form more strong linkages with amino groups. Attributing to these two features, C. I. Direct Blue 71 showed greater substantivity towards chitosan treated fabric.

A normal cotton fabric when entered in dye bath acquires negative surface charge and repels negatively charged dye anions. Conventionally, the negative charge is neutralized by the addition of electrolytes such as sodium chloride, sodium sulphate etc and facilitate approach of direct dyes, by their inherent affinity, towards fibre. The polycationic chitosan can also dissipate the negative surface charge on cotton and drives dye molecules to the fibre. Such effects can be studied by comparing the dyeing results of chitosan treated samples conducted in electrolyte free dye bath with that in presence of electrolyte. The progressive decrease in importance of sodium sulphate taken as electrolyte with increase in chitosan concentration, as shown in Table 2.23 (Figure 2.22

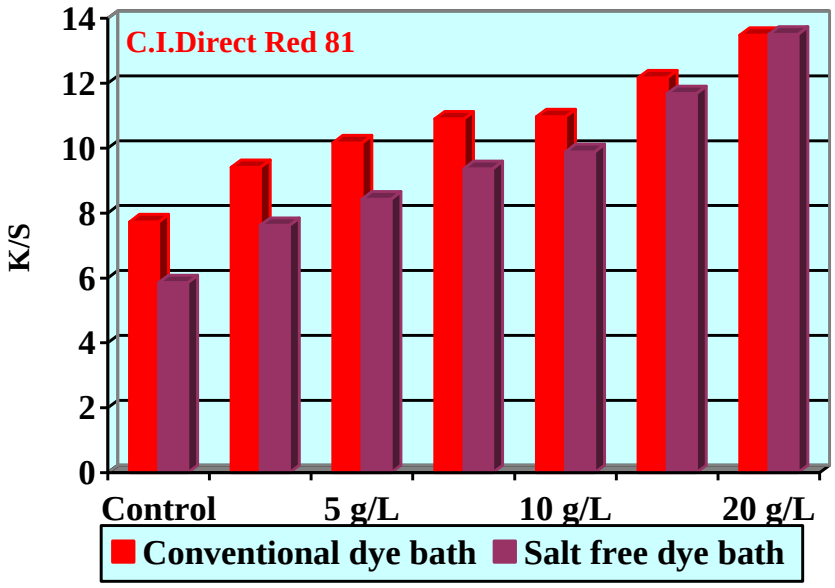
and Figure 2.23), clearly elucidates the role of chitosan in the improvement of dye uptake even at reduced electrolyte concentration.

Table 2.23 Effect of electrolyte (sodium sulphate) on dyeing of chitosan (CHT) treated cotton fabric

CHT, g/L	**K/S values**			
	C.I.Direct Red 81		**C.I. Direct Blue 71**	
	Conventional dye bath	**Salt free dye bath**	**Conventional dye bath**	**Salt free dye bath**
Control	7.73	5.86 *[-24]*	7.41	5.48 *[-26]*
2.5	9.41	7.62 *[-19]*	9.60	7.49 *[-22]*
5.0	10.16	8.43 *[-17]*	10.81	8.86 *[-18]*
7.5	10.90	9.37 *[-14]*	11.60	9.98 *[-14]*
10.0	10.97	9.89 *[-12]*	12.42	10.78 *[-13]*
15.0	12.17	11.68 *[-4]*	15.64	15.17 *[-3]*
20.0	13.48	13.51 *[+0.2]*	16.05	15.98 *[-0.4]*

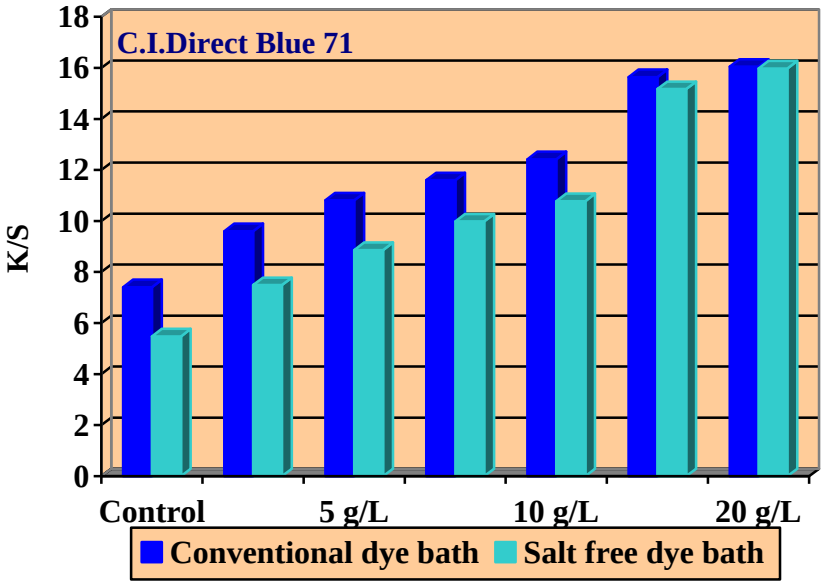
Dye 1% o.w.m, Values in brackets indicate % change in colour value form corresponding conventional dyed samples; -ve sign indicate decrease in colour depth

C. I. Direct Red 81 dye has shown poor washing fastness ratings which may be attributed to its low molecular weight and the poor substantivity due the lesser conjugation as can be seen from its structure (Table 2.1). The fastness of this dye on chitosan treated fabric, as observed from Table 2.24, is improved slightly with increase in concentration of chitosan, particularly in case of relatively low molecular weight chitosan treated samples. On the other hand a slight decline in ratings with increase in concentration of high molecular weight chitosan is noticed. This may be attributed to the preferential surface deposition of high molecular weight chitosan and hence the dye also that may be removed easily during washing. However, the effect of chitosan treatment on washing fastness of dyes having good washing fastness, i.e. C. I. Direct Blue, is only slightly altered, Table 2.25.



Dye 1% o.w.m.

Figure 2.22 Effect of electrolyte (sodium sulphate) on dyeing of chitosan (CHT) treated cotton fabric with C. I. Direct Red 81



Dye 1% o.w.m.

Figure 2.23 Effect of electrolyte (sodium sulphate) on dyeing of chitosan (CHT) treated cotton fabric with C.I. Direct Blue 71

Table 2.24 Effect of chitosan pretreatment on fastness properties of direct dye C.I.Direct Red 81

Conc, g/L	Washing fastness ratings of C.I.Direct Red 81 dyed samples pretreated with:						
	CHT-MC (654,127)	**CHT-D1 (285,231)**	**CHT (135,839)**	**CHT-D2 (71,676)**	**CHT-D3 (38,733)**	**CHT-D4 (20,698)**	**CHT-D5 (11,986)**
5.0	2-3	2-3	2-3	3	3	3	3
10.0	3	3	3	3	2-3	3-4	3-4
15.0	2-3	3	3-4	3-4	3-4	3-4	3-4
20.0	2	3	3	2-3	3-4	3-4	3-4
	Rubbing fastness ratings						
5.0	2	2	2	2	2-3	2-3	2-3
10.0	2	2	2	2	2-3	2-3	2-3
15.0	1-2	1-2	2	2	2	2	2
20.0	1-2	1-2	1-2	2	2	2	2

Values in parentheses indicate the mol wt of chitosan,
Dye 1% o.w.m., ratings of control samples: washing fastness 3 and rubbing fastness 2-3

Table 2.25 Effect of chitosan pretreatment on fastness properties of direct dye C.I. Direct Blue 71

Conc, g/L	Washing Fastness Ratings of C.I.Direct Blue 71 dyed samples pretreated with:						
	CHT-MC (654,127)	**CHT-D1 (285,231)**	**CHT (135,839)**	**CHT-D2 (71,676)**	**CHT-D3 (38,733)**	**CHT-D4 (20,698)**	**CHT-D5 (11,986)**
5.0	4-5	4	4-5	4-5	4	4-5	4-5
10.0	4	4-5	4-5	4	4-5	4-5	4
15.0	4	4-5	4-5	4	4-5	5	4-5
20.0	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	Rubbing fastness ratings						
5.0	2	2	2	2	2-3	2-3	2-3
10.0	2	2	2	2	2-3	2-3	2-3
15.0	1-2	1-2	2	2	2	2	2
20.0	1-2	1-2	1-2	2	2	2	2

Values in parentheses indicate the mol wt of chitosan,
Dye: 1% o.w.m, ratings of control samples: washing fastness 4-5 and rubbing fastness 2-3

The rubbing fastness, as can be seen from the above tables, reduced with the increase in the molecular weight and concentration of chitosan in the treatment bath. This may be due to surface deposition of chitosan that can be easily rubbed off.

2.3.13.2 Effect of chitosan treatment on colour depth of direct dyed cotton fabric

Chitosan, with due regards to its several inherent properties, can be employed as finishing agent and may be required to apply onto dyed fabrics. Chitosan, due presence of

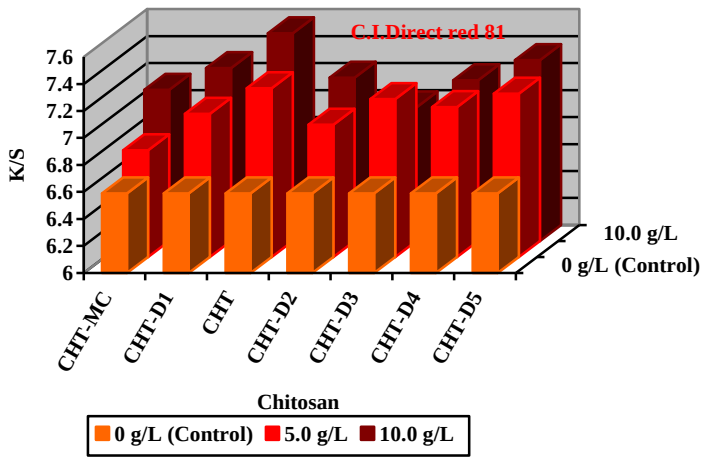
various functional groups, is believed to interact with the dyes present on fibre and alter their properties. In this study, cotton fabric was dyed separately with direct dyes namely C. I. Direct Red 81 and C. I. Direct Blue 71 of 1% shade by conventional dyeing method. The dyed fabric was then treated with chitosan solution by pad-dry cure method.

Table 2.26 Effect of chitosan treatment on colour depth and fastness of direct dyed cotton fabric

Sample	Chitosan, g/L	C. I. Direct Red 81			C.I. Direct Blue 71		
		K/S Values	Washing Fastness	Rubbing Fastness	K/S Values	Washing Fastness	Rubbing Fastness
Control	-	6.59	3	2-3	7.29	4-5	2-3
CHT-MC Treated	5	6.79 *[3.0]*	3	3	7.24 *[-0.7]*	4	3
	10	7.12 *[8.0]*	3-4	3	7.49 *[2.7]*	4-5	3
CHT-D1 Treated	5	7.06 *[7.1]*	3-4	3	7.19 *[-0.1]*	4-5	3
	10	7.28 *[10.5]*	3-4	3	7.33 *[0.6]*	4-5	3
CHT Treated	5	7.25 *[10.0]*	3-4	2-3	6.83 *[-6.3]*	4-5	3
	10	7.54 *[14.4]*	3-4	3	7.31 *[0.3]*	4	3
CHT-D2 Treated	5	6.98 *[5.9]*	3-4	2-3	6.75 *[-7.4]*	4-5	3
	10	7.21 *[9.4]*	3-4	3	7.02 *[-3.7]*	4-5	3
CHT-D3 Treated	5	7.17 *[8.8]*	3-4	2-3	6.59 *[-9.6]*	4-5	3
	10	6.99 *[6.1]*	4-5	2-3	6.62 *[-9.2]*	4-5	3
CHT-D4 Treated	5	7.11 *[7.9]*	4	2-3	6.64 *[-8.9]*	4-5	2-3
	10	7.19 *[9.1]*	4	2-3	6.81 *[-6.6]*	5	3
CHT-D5 Treated	5	7.21 *[9.4]*	4	2-3	6.71 *[-7.9]*	4-5	2-3
	10	7.34 *[11.4]*	4-5	2-3	6.74 *[-3.4]*	5	2-3

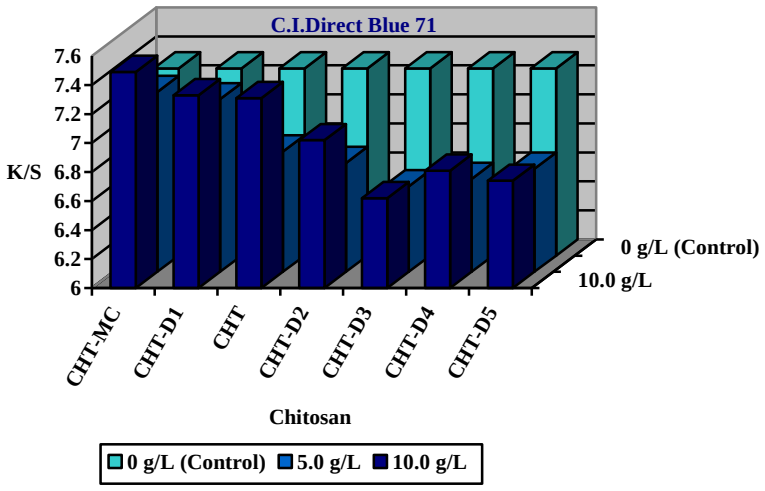
Dye 1% o.w.m, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986,
Values in bracket indicate the per cent change in colour value compared to control sample

Table 2.26 (Figure 2.24 and Figure 2.25) shows that the colour value of C. I. Direct Red 81 improved whereas that of C.I. Direct Blue 71 decreased by the chitosan after treatment, nevertheless to very small extent. Any regular trend on the colour depth, however, is not noticed due to the molecular weight of treated chitosan. In all cases, the bloom is somewhat enhanced at higher concentration treatment. In case of red dyed samples, blooming is on higher side on high molecular weight chitosan treated samples whereas low molecular weight showed somewhat lesser but almost similar level of blooming. In blue dyed samples, the colour change was negligible when treated with high molecular weight chitosan and the loss in colour value was observed in low molecular weight chitosan treated samples. The apparent changes in shade may be attributed to the migration of dye from the fibre phase to the chitosan phase during padding and subsequently during drying operations due to the interaction of the anionic sulphonate group of dye with cationic groups of chitosan. The higher dye migration of C.I. Direct Red 81 may be attributed to its low molecular weight and poor washing fastness. The washing fastness of post dyeing chitosan derivative treatment was improved to some extent. This may be attributed to the complex formation between dye and the chitosan. Rubbing fastness, however, was not significantly altered.



Dye 1% o.w.m, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.24 Effect of chitosan treatment on colour depth of direct dyed cotton fabric



Dye 1% o.w.m, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.25 Effect of chitosan treatment on colour depth of direct dyed cotton fabric

2.3.13.3 Effect of chitosan pretreatment on acid dyeing of cotton fabric

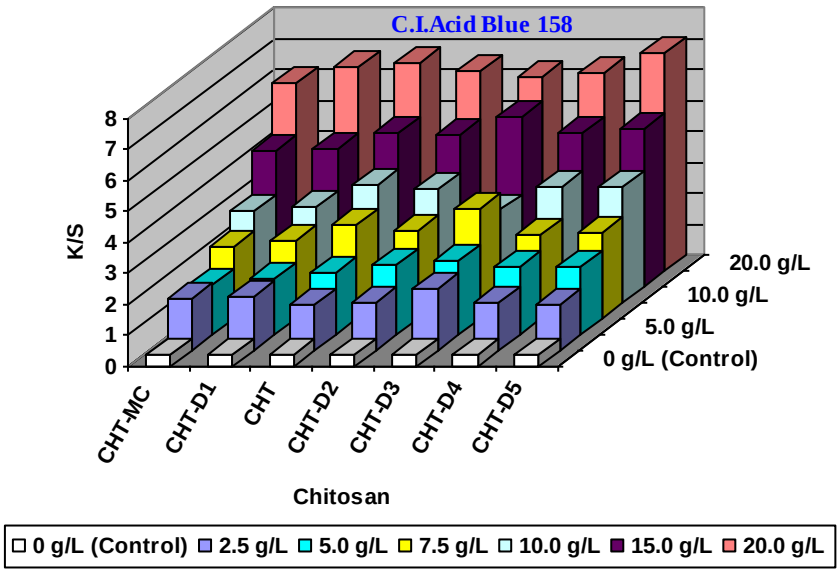
Chitosan possesses one amino group in its glucosamine unit, which forms positive charge in presence of acid. This positively charged amino group can form salt linkage with anions. To characterize the chitosan treated fabric, the work was extended further to investigate its dyeability towards acid dye (C.I. Acid Blue158), which is non dyeable towards normal cotton. The results are presented in Table 2.27 and graphically in Figure 2.26.

Table 2.27 Effect of chitosan treatment on acid dyeing

Conc, g/L	K/S values of C.I. Acid Blue 158 dyed samples pretreated with:						
	CHT-MC (654,127)	CHT-D1 (285,231)	CHT (135,839)	CHT-D2 (71,676)	CHT-D3 (38,733)	CHT-D4 (20,698)	CHT-D5 (11,986)
2.5	1.70	1.72	1.47	1.56	2.01	1.54	1.49
5.0	1.61	1.81	2.02	2.28	2.37	2.18	2.19
7.5	2.33	2.53	3.01	2.82	3.55	2.69	2.78
10.0	2.99	3.12	3.83	3.69	3.01	3.77	3.73
15.0	4.40	4.45	4.94	4.90	5.49	4.96	5.09
20.0	6.09	6.59	6.70	6.47	6.26	6.36	7.01

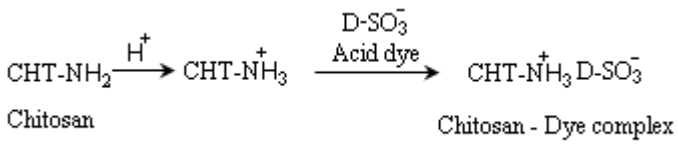
Dye 2% o.w.m, K/S values of control sample is 0.38; Values in parentheses indicate the mol wt of chitosan

It was revealed from these demonstrations that the chitosan derivatives treated cotton fabrics dyed substantially with acid blue158 as against only a tint on control and remained fast to hard soaping. A progressive increase in dye up take was observed with increase in concentration of respective chitosan. The dye uptake, however, was almost identical by the samples when treated with varying molecular weight chitosan at any particular concentration. This kind of dyeability can be purely attributed to the binding of acid dye to chitosan by salt linkages as shown in scheme 2.2. Thus, the dyeability toward acid dye can be taken as one of the characterization test for the retention of chitosan on cotton fabric and the progressive increase in dye uptake corresponds to the number of protonated amino groups of chitosan present on treated cotton fabric forming ionic linkage with stoichiometric amount of anionic acid dye.



Dye 2% o.w.m, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.26 Effect of chitosan pretreatment on acid dyeing



Scheme 2.2 Reaction of chitosan with acid dye

2.3.14 Effect of chitosan treatment on wrinkle recovery property of cotton fabric

The aesthetic appeal of cotton cloth or garments is severely affected due to its creasing tendency. Creasing in cotton fabrics occurs due to the bonding of free hydroxyl groups, present in the amorphous regions, through hydrogen bonds when pressed or folded. Thus the creasing behaviour of cotton may be directly associated with the ability of free hydroxyl groups in amorphous region to get bound to each other. The creasing problem can, therefore, be minimized by blocking or masking these hydroxyl groups by means of cross linking of hydroxyl groups of adjacent cellulose macromolecules. Crosslinking agent based on aminoplast resins, e.g. dimethylol dihydroxy ethylene urea (DMDHEU) are commercially employed easy care finishing of cotton, Figure 2.27 [25, 26]. The performance of DMDHEU and various grades of chitosan in terms of crease recovery angle in easy care finishing of cotton are illustrated in Table 2.28 and Table 2.29 respectively. DMDHEU was applied onto cotton fabric by pad-dry cureprocess using magnesium chloride as catalyst and acetic acid.

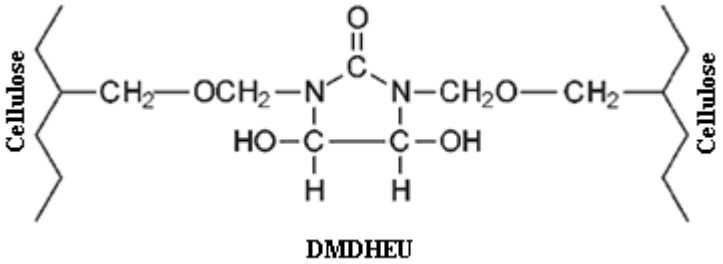


Figure 2.27 Crosslinking of cellulose macromolecules by DMDHEU

Compared to commercial cross linking agent DMDHEU treatment, Table 2.28; the wrinkle recovery of chitosan treated cotton fabrics was not satisfactory, Table 2.29. There was tremendous decline in CRA with increase in concentration of chitosan. However, there is slight improvement in wrinkle recovery by lowering the molecular weight especially for chitosan applications at low concentrations. The high molecular weight chitosan is believed to form a surface coating thus ignoring the possibility of cross linking. Therefore, stiff film formed may deform almost permanently when stressed. This may be the fundamental reason for low CRA values for any stiff finishes. In order to

minimize the loss in resiliency, addition of commercial cross linking agents to the pad bath formulation is recommended, Table 2.30.

Table 2.28 Wrinkle recovery property of DMDHEU treated cotton fabric

DMDHEU, g/L	Crease Recovery Angle^o		
	Warp	Weft	Total
Control	80	81	161
20	85	95	180
40	106	101	207
60	112	113	215
80	114	112	226
100	119	123	233

Pad liquor: $MgCl_2$ 10 g/L, Acetic acid 15 ml/L; Curing temp/time 150 ^{0}C/4min

Table 2.29 Wrinkle recovery property of chitosan treated cotton fabric

Conc, g/L	Crease Recovery Angle^o of cotton fabrics pretreated with:						
	CHT-MC (654,127)	CHT-D1 (285,231)	CHT (135,839)	CHT-D2 (71,676)	CHT-D3 (38,733)	CHT-D4 (20,698)	CHT-D5 (11,986)
2.5	137	140	140	140	176	167	170
5.0	143	140	140	160	164	163	164
7.5	129	128	119	152	141	151	152
10.0	94	108	125	138	128	140	144
15.0	96	98	110	127	134	141	140
20.0	90	91	98	116	121	138	139

Values in parentheses indicate the mol wt of chitosan, CRA of control sample 161^o

Table 2.30 Wrinkle recovery property of chitosan and DMDHEU treated cotton fabric

DMDHEU concentration, g/L	Crease Recovery Angle^o		
	DMDHEU treated	DMDHEU + CHT (10 g/L) treated	DMDHEU + CHT (20 g/L) treated
20	180	153	134
40	207	163	139
60	215	177	158
80	226	191	170
100	233	198	179

Pad liquor: $MgCl_2$ 10 g/L, Acetic acid 15 ml/L; Curing temp/time 150 ^{0}C/4 min, CRA of control sample is 161^0, CHT (10g/L) treated 125^0, CHT (20g/L) treated 98^0

2.3.15 Effect of chitosan treatment on resistance against microorganism of cotton fabric

Textile products made out of natural fibres provide favourable environment for the growth of microorganisms (algae, fungi, bacteria etc), due to moisture and warmth. These organisms are mainly responsible for discolouration, stains, strength loss etc of fabric and skin allergies, infection diseases etc to human body [42, 99-101]. The rancid smell is produced when bacteria that are present on the skin work on sweat and decompose it. The decomposition products that are responsible for odour are ammonia, methyl amine, hydrogen sulphide, low molecular weight fatty acids, urea etc [102-104]. Antimicrobial finishes can give rise to hygienic freshness and also can be used to fight against pathogenic and parasitic microorganism. Antimicrobial agents either inhibit the growth (-static) or kill (-cidal) the microorganism. Using number of chemicals such as organo-metallics, phenols, thiophenols, formaldehyde derivatives and several quaternary ammonium compounds, microbial growth can be inhibited. These chemicals, however, are non biodegradable and toxic. Some of the commercial antimicrobial textile products currently marketed are: Biogaurd produced by Aegis Environments (formerly Dow Corning) is quaternary ammonium compound, namely, 3-trimethoxy silyl propyldimethyl octadecyl ammonium chloride, Reputex 20 (Arch Chemicals) is polyhexamethylene biguanide, Triclosan (2,4,4'-trichloron2'-hydroxydiphenyl ether) etc. Environmental issues of these products are still of concern [26, 99]. Cotton fabric with good antimicrobial activity is obtained by using chitosan, which is attributed to the amino groups that are present on chitosan macromolecule. Thus the degree of deacetylation, molecular weight and concentration of chitosan influence the antimicrobial activity **[**1]. The antimicrobial properties of chitosan and its derivatives are studied in present and subsequent chapters.

The composted soil bed composed of variety of microbes (e.g. bacteria and fungi) can be employed in soil burial test. The microbial attack of cellulolytic microflora in a composted soil bed is considered to be the most rigorous and practical means for the evaluation of anti deterioration treatments. The treated and untreated fabric strips are buried and exposed to the microbial attack (cellulolytic microflora) for a stipulated period. The change in fibre strength (tenacity) of the sample during incubation is taken as

a measure of the effectiveness of the biocide compound [105]. The effect of different molecular weight grades of chitosan treatment on cotton fabric for resistance against microbial attack was studied. Similar study was conducted on chitosan treated dyed fabrics i.e. post dyeing chitosan treated.

Table 2.31 Effect chitosan treatment on resistance against microbial attack of cotton fabric (soil burial test)

Sample	Tenacity, g/tex		Drop in strength, %	Elongation at break, %	
	Before soil burial	After soil burial		Before soil burial	After soil burial
Untreated cotton fabric	23.33	18.98	18.65	5.25	3.50
Control	20.87	18.08	22.50	5.00	3.50
CHT-MC	22.02	19.38	11.98	5.00	3.50
CHT-D1	21.87	19.07	12.76	4.50	3.5
CHT	21.77	18.64	14.36	4.5	3.75
CHT-D2	21.87	18.83	13.90	4.5	3.75
CHT-D3	22.03	19.00	13.75	4.5	3.75
CHT-D4	21.88	18.75	14.31	4.5	3.5
CHT-D5	22.01	18.51	15.90	4.5	3.5

Conc of chitosan derivatives in pad liquor 10 g/L, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

It was observed from Table 2.31 that the tenacity of cotton fibres decreased due hydrolytic degradation during blank treatment with acetic acid and curing at elevated temperature. The fibre strength was restored significantly by the treatment chitosan. The effect of molecular weight of chitosan on tensile properties of cotton fibre was found to be of almost identical level. The higher molecular weight chitosan, however, showed somewhat better strength fibre. This improvement may be attributed to the load bearing capacity of rigid film anchored over the fibre surface. The rigidity of high molecular weight chitosan and interaction of aldehyde end groups of anhydromannitol on depolymerized chitosan with cellulose may probably be the contributing factor in strength determination [37]. The undyed and dyed untreated cotton fabrics, as revealed from Table 2.31 and Table 2.32 (Figure 2.28), were more prone to microbial attack of cellulolytic microflora in a composted soil bed. The less loss in tenacity of fibre means better resistance against microbes. The blank treated samples, both undyed and dyed,

showed maximum strength loss followed by untreated samples. Samples treated with chitosan were found to be more resistant to microbial attack as manifested by the lesser drop in strength. In case of undyed fabric, with increase in the molecular weight of chitosan, the strength loss was found to be progressively decreased. Further, the dyed fabrics treated with chitosan were slightly more susceptible for microbial attack in soil burial test. The elongation capacity of fibre was also found to be affected due to rotting; nevertheless the extent was almost of same level for all chosen grades of chitosan, Table 2.31.

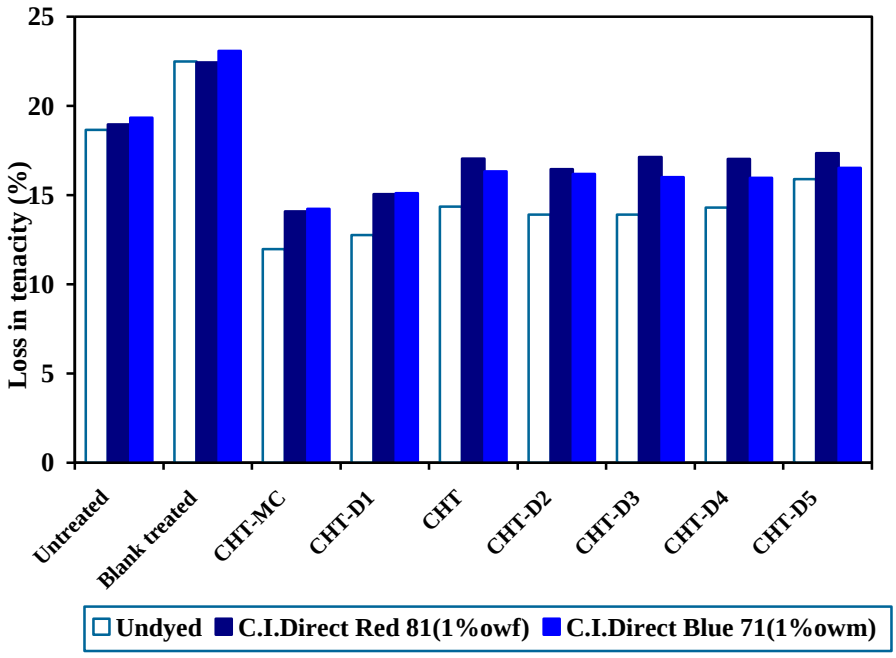
Table 2.32 Effect chitosan treatment on resistance against microbial attack of dyed cotton fabric (soil burial test)

Sample	C.I. Direct Blue 71			C. I. Direct Red 81		
	Tenacity, g/tex		Drop in strength, %	Tenacity, g/tex		Drop in strength, %
	Before soil burial	After soil burial		Before soil burial	After soil burial	
Dyed Untreated	22.68	18.32	19.33	22.73	18.42	18.96
Dyed (Blank treated)	20.66	15.89	23.08	20.81	16.14	22.43
CHT-MC	21.86	18.75	14.23	21.72	18.66	14.09
CHT-D1	21.72	18.44	15.10	21.41	18.19	15.04
CHT	21.59	18.06	16.33	21.14	17.95	17.04
CHT-D2	21.69	18.18	16.18	21.20	17.71	16.46
CHT-D3	21.36	17.94	16.01	21.25	17.61	17.13
CHT-D4	21.54	18.10	15.97	21.04	17.46	17.02
CHT-D5	21.41	17.87	16.53	21.50	17.77	17.35

Dye 1%, o.w.m, Conc of chitosan derivatives in pad liquor 10g/L, Blank treatment was given with acetic acid 15 ml/L, sodium acetate 10 g/L by pad-dry cure method, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

The susceptibility of blank treated samples to microbial attack may be probably due to the acid hydrolytic degradation occurred during thermo curing. The mode of interaction between chitosan, its derivatives and the microorganism may be considered to be the combination of different mechanisms. Chitosan believed to form a rigid film over the fibre surface that share the load and also act as a protective layer against microbes during rotting. Increased losses in strength due to rotting in case of low molecular weight

chitosans may be due to the greater permeability for microorganisms due to more opened surface as can be observed from SEM, Figure 2.14 (e & f).



Dye 1% o.w.m., Conc of chitosan derivatives in pad liquor 10 g/L, blank treatment was given with acetic acid 15 ml/L, sodium acetate 10 g/L by pad-dry cure method; Mol wt of chitosan grades: CHT -MC=654,127, CHT-D1=285,231, CHT=135,839, CHT-D2=71,676, CHT-D3=38,733, CHT-D4=20,698 and CHT- D5=11,986

Figure 2.28 Effect chitosan treatments on resistance against microbial attack of cotton fabric

Secondly, due to their polycationic nature, chitosan exhibit inherent antimicrobial properties. The cell wall of most of the microbes is a polysaccharide composed of lipopolysaccharide and/or peptidoglycan both having an ionic group due to the presence of phosphates, carboxylates, *N*-acetylmuramic acid etc that can interact with poly cations of CHT derivatives. This cell wall maintains the integrity of cellular components and shields the cell from the extracellular environments. Immediately beneath the cell wall is a semi- permeable membrane which encloses intracellular organelles and a myriad of enzymes and nucleic acid. The enzymes are responsible for the chemical reactions that take place within the cell, and the nucleic acids store all the genetic information of the organism. The survival or growth of microorganisms depends on the integrity of the cell and the concerted action and proper state of all these components. It is believed that the

polycationic nature of chitosan initiates binding with the cell membrane by means of electrostatic attraction with negatively charged microbial cell membrane. Once bound to the cell surface, chitosan is thought to affect membrane permeability which results into the leakage of proteinaceous material and other intracellular constituents of the microbial cell causing death due to the loss of essential fluids [99, 106, 107]. Chitosan is also observed to bind DNA and inhibit mRNA and protein synthesis. Low molecular weight chitosan is more effective as it penetrates deeper into the cell of microorganisms [108, 109]. Due to chelation property, chitosan also binds trace of essential metal ions present in the intracellular fluid. Deficiency of such metal ions may inhibit production of toxins, enzymes and the microbial growth [110].

2.3.16 Pad-dry-alkali process

Application of chitosan by pad-dry cure process has faced certain challenges particularly of moisture related and drape. The treated fabrics acquired undesired stiffness and lost the inherent cotton feel and the absorbency was affected to some extent. In order to overcome such limitations, an attempt was made to modify the process. Chitosan is soluble in acidic medium and precipitates in alkaline and this principle was employed in pad-dry alkali method. This process is the combination of exhaust and padding method and thermal energy is conserved. Fabric was treated with acidic chitosan solution in presence of sodium acetate, as viscosity modifier, for thirty minutes and then passed through padding rollers. The treated fabric was air dried and soaked in sodium hydroxide solution for ten minutes so that chitosan particles can be deposited in situ of the fibre. The fabric was then washed thoroughly, dried and hot pressed. The surface morphology of the cotton fibres treated with chitosan by pad-dry-alkali process, as observed in SEM, is shown in Figure 2.29. The surface deposition of chitosan on fibre can be easily visualized from SEM of treated samples. A rough surface together with some discrete particles is the evidence of chitosan deposition on surface. Swelling of fibres to some extent is also seen when treated with low molecular weight chitosan.

Table 2.33A and Table 2.33B present various properties of CHT and CHT-D5 treated fabrics by pad-dry -alkali process.

Table 2.33A Properties of chitosan treated cotton fabric by pad-dry-alkali process

Properties	Control	Pad - dry cure process, 2.5g/L		Pad - dry- alkali process, 2.5 g/L	
		CHT Treated	CHT-D5 Treated	CHT Treated	CHT-D5 Treated
Whiteness Index,	*92.5*	91.5	89.3	92.5	92.4
Bending length, cm	*2.05*	2.44	2.13	2.08	2.06
Absorbency, sec	*4.02*	4.54	4.18	4.22	4.09
Dye up take, K/S					
C.I.Direct Red 81	*7.73*	9.41 [22]	9.36 [21]	9.47	9.51
C.I.Direct Blue 71	*7.41*	9.60 [30]	9.34 [26]	9.77	9.63
C.I. Acid Blue158	*0.38*	1.47	1.49	1.70	1.58
Washing fastness					
C.I.Direct Red 81	*3*	2-3	3	2-3	2-3
C.I.Direct Blue 71	*4-5*	4-5	4-5	3-4	3-4
CRA^0	161	140	170	138	126

Values in brackets indicate the change in colour value from control

Table 2.33B Properties of chitosan treated cotton fabric by pad-dry-alkali process

Properties	Control	Pad - dry- cure process, 10 g/L		Pad - dry- alkali process, 10/L	
		CHT Treated	CHT-D5 Treated	CHT Treated	CHT-D5 Treated
Whiteness Index,	92.5	91.4	86.2	92.3	92.3
Bending length, cm	2.05	3.70	2.71	2.32	2.26
Absorbency, sec	4.02	7.20	5.41	5.06	4.11
Dye up take, K/s					
C.I.Direct Red 81	*7.73*	10.97 [42]	11.09 [43]	11.43	11.21
C.I.Direct Blue 71	*7.41*	12.42 [68]	13.08 [77]	12.38	12.88
C.I. Acid Blue158	*0.38*	3.83	3.73	3.95	3.81
Washing fastness					
C.I.Direct Red 81	*3*	3	3-4	2-3	2-3
C.I.Direct Blue 71	*4-5*	4-5	4	3-4	3-4
CRA^0	161	125	144	128	134

Values in brackets indicate the change in colour value from control

The whiteness index was very much close to that of control. The stiffness was lower than that was observed with counterpart in pad-dry cure method. Absorbency and dyeing results were superior to curing method. This method, however, was not suitable for the treatment of post dyed fabrics due to heavy bleeding of dye. The fastness to washing of chitosan treated by pad-dry-alkali process and then dyed samples was unsatisfactory. Wrinkle recovery property was also affected severely.

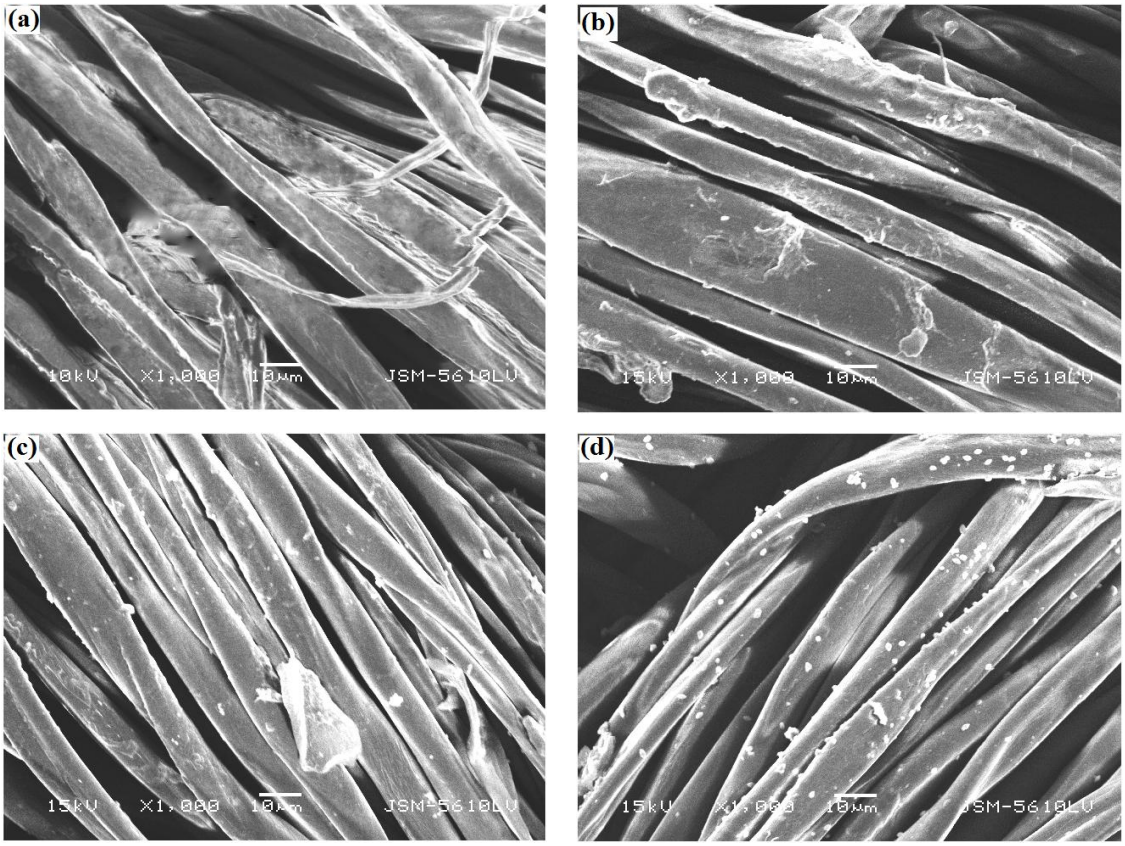


Figure 2.29 Scanning electron microphotographs chitosan treated samples by pad-dry-alkali method (x1000) (a) Cotton Fibre (control), (b) CHT-MC treated fibres, (c) CHT treated fibres and (d) CHT-D5 treated fibres

REFERENCES

1. S. Sudha, V.R. Giridev, R. Neelkandan and M.S. Kumar, "Chitosan. - A versatile polymer for textile applications", *Journal of the Textile Association,* **64** (4), Nov-Dec (2006) 165-166

2. S. Hirano, "Chitin and hitosan" in *Ullmann's Encyclopaedia of Ind. Chemistry,*

Vol. 7, 6th Ed, Wiley-VCH, Weinheim(Germany), (2003) 679-691

3. H. Struszczyk, O. Kivekas, A. Niekraszewicz and A. Urbanowski, "Chitosan-new forms and uses", *Textile Asia*, July(1993)80-83
4. S. Ghosh, and M. Jassal, "Use of polysaccharide fibres for modern wound dressing", *Indian Journal of Fibre & Textile Research*, **27,** Dec (2002) 434-450
5. Kadriye Tuzlakoglu, Catarina M. Alves, Joao F. Mano and Rui L. Reis, "Production and characterization of chitosan fibers and 3-D fiber mesh scaffolds for tissue engineering applications", *Macromolar Bioscience*, **4** (2004) 811–819
6. V.R. Giri Dev, R. Neelkandan, N. Sudha,,O.L. Shamugasundaram and R.N. Nadaraj, "Chitosan- A polymer with wider applications", *Textile Magazine,* July (2005) 83-86
7. Yimin Qin, "Gelling fibres from cellulose, chitosan and alginate", *Chemical Fibres International*, **58**(1)March (2008)30-32
8. http://www.swicofil.com/products/055chitosan
9. Lalit Jajpura, Ajay Harad and Satarup Maitra, "Chitin and chitosan in antimicrobial composite fibres", *Asian Textile Journal,* **15** (2), Feb(2006) 55-58
10. N. Streiner, "Evaluation of peracetic acid as an ecofriendly safe alternative for hypochlorite", *Textile Chemists and Colorists*, **27** (1995) 29-32
11. M. Hashem, "Catalytic activation of per acetic acid using chitosan-metal complex for low temperature bleaching of cotton", *Indian Journal of Fibre & Textile Research,* **28,** Dec (2003) 444-449
12. D.P.Chattopadhyay, "Cationization of cotton for low salt and salt free dyeing ", *Indian Journal of Fibre & Textile Research*, **24**, March (2001)108-115
13. V.R. Giridev, M. Senthil Kumar, R. Neelkandan and M. Murugesan, "Effect of chitosan treatment on cotton fabric dyeing", *Indian Textile Journal,* March (2004) 29-31
14. B. N. Bandyopadhyay, G. N. Sheth, and M. M. Moni, "Chitosan can cut salt use in reactive dyeing", *International Dyer*, **183**(11), 39-42 (1998)
15. Sang –Hoon Lim and Samuel Hudson, "Application of fibre-reactive chitosan derivative to cotton fabric as a zero salt dyeing auxiliary", *Coloration*

Technology, **120** (2004) 108-113

16. T. Kavitha, R. Padmashwini, A. Swarna, V.R. Giri Dev, R. Neelkandan and M. Senthil Kumar, "Effect of chitosan treatment on the properties of turmeric dyed cotton yarn", *Indian Journal of Fibre & Textile Research*, **32**, March (2007) 53-56
17. R. D. Metha and R. N. Combs, "An improved process for nep coverage in dyeing cotton", *American Dyestuffs Reporter*, **80**(9), (1991) 74-79
18. J. A. Rippon, "Improving the dye coverage of immature cotton fibres by treatment with chitosan", *Journal of Society of Dyers Colourists*, **100** (1984) 298-303
19. Shadi Houshyar and Hossein Amirshahi, "Treatment of cotton with chitosan and its effect on dyeability with reactive dyes", *Iranian Polymer Journal*, **11**(5), (2002) 295-301
20. N. Sekar, "Chitosan in textile processing-an update", *Colourage*, **XLVII** (7) July (2000) 33-34
21. S.K. Tiwari, K.G. Prajapati, and M.M. Gharia, "Pigment prints and antibacterial characteristics", *Colourage*, **XLVIII** (2001)17-20
22. S.A. Bahmani, G.C. East, and I.J. Holme, *Journal of Society of Dyers and Colourists*, "The application of chitosan in pigment printing ", **116,** March (2000) 94-98
23. Siriwan Kittinaovarat and Pariya Kantuptim, "Comparable antibacterial properties of glyoxal and glyoxal-chitosan treated cotton fabrics", *AATCC Review*, April (2005) 22-24
24. C.W.M. Yuem, S.K.A. Ku, C.W. Kan and P.S.R. Choi, "Enhancing textile inkjet printing with chitosan", *Coloration Technology*, **123** (2007) 267-270
25. V.A.Shenai and N.M. Saraf, *Technology of Finishing*, Vol-X, Sevak Publications, Mumbai, India (1987)
26. W.D. Schindler and P.J. Hauser, *Chemical finishing of textiles*, Woodhead Publishing Limited, Cambridge, England, (2004)
27. E. J. Blanchard, R. M. Reinhardt, and B. A. K. Andrews, "Finishing with modified polycarboxylic acid systems for dyeable durable press cottons", *Textile*

Chemists and Colorists, **23**(5), 25-28 (1991)

28. A.Hebeish, A.Waly and A.Aou-Okeil, "The effect of molecular weight of chitosan on cotton fabric treated with citric acid and its impact on dyeing with some acid dyes", *Journal of the Textile Association,* **65** (5), Jan-Feb (2005) 219-227
29. Kh.F.El.Tahlawy, "Utilization of citric acid – chitosan, sodium hypophosphite system for effecting concurrent dyeing and finishing", *Colourage*, **XLVI** (5) (1999) 21-26
30. Y.S. Chung, K.K. Lee, and J.W. Kim, "Durable press and antibacterial finishing of cotton fabrics with citric acid and chitosan treatment", *Textile Research Journal*, **68** (10) (1998) 772-775
31. K. S. Huang, W. J. Wu, J. B. Chen and H. S. Lian, "Application of low-molecular-weight chitosan in durable press finishing", *Carbohydrate Polymers*, **73**, (2008) 254–260
32. P. Shyam Sundar, S. Tamilarasan, T. Sridhar, and P.C. Shobhana Shree, "Chitosan citrate -an eco friendly resin for cotton fabric", *International Dyer*, **192** (2), March (2001) 32-35
33. N. Bhattacharyya, B. A. Doshi, A. S. Sahasrabudhe, and P. R. Mistry, "Use of chitosan in dyeing and finishing of cotton fabric", in *Resume of Papers, 34th Joint Technological Conference of ATIRA, BTRA, SITRA, and NITRA*, (1993)115-121
34. D.P.Oultan , "Fire retardant textile" in *Chemistry of the Textile Industry*, C.M. Carr (ed) 1st ed, Chapman & Hall, London, (1995)102-124
35. G.P. Nair, "Development of flame retardant finish for cotton sarees", *Colourage*, **XLVII** (5) (2000) 21-26
36. Khaled El-Tahlawy, Roshdi Eid, Fawzy Sherif and Samuel Hudson, "Chitosan: A new route for increasing the efficiency of stannate/phosphate flame retardants on cotton", *Journal Textile Institute,* **99** (2) (2008) 157-164
37. Ha-Soo Seaong, Jae-Pil Kim and Sohk- Won Ko, "Preparing chito-oligosaccharide as antimicrobial agents for cotton", *Textile Research Journal,* **69** (7) July (1999) 483-488

38. S.W. Fang, C.F. Li, and D.Y.C. Shih, "Antifungal activity of chitosan and its preservative effect on low-sugar candied kumquat", *Journal of Food Protection*, **56**(2) (1994)136-140

39. G.J. Tsai and W.H. Su, "Antibacterial activity of shrimp chitosan against *Escherichia coli*", *Journal of Food Protection*, **62**(3) (1999) 239-243

40. N.R. Sudardshan, D.G. Hoover, and D. Knorr, "Antibacterial action of chitosan", *Food Biotechnology* , **6**(3), (1992) 257-272

41. G.-H. Wang, "Inhibition and inactivation of five species of food borne pathogens by chitosan", *Journal of Food Protection*, **55**(11), (1992) 916-919

42. Daniela Enescu, "Use of Chitosan in Surface Modification of Textile Materials", *Roumanian Biotechnological Letters* , **13** (6) (2008) 4037-4048

43. W.J. Ye, M.F. Leung, J. Xin, T.L. Kwong, D.K.L. Lee and P. Li, "Novel core-shell particles with poly(n-butyl acrylate) cores and chitosan shells as an antibacterial coating for textiles", *Polymers*, **46** (2005)10538-10543

44. Weijun Ye, John H. Xin, Pei Li, Kam-Len Daniel Lee, Tsz-Leung Kwong, "Durable antibacterial finish on cotton fabric by using chitosan-based polymeric core-shell particles", *Journal of Applied Polymer Science*, **102** (2) October (2006) 1787–1793

45. M. L. Joseph, *Introductory Textile Science*, 5th Ed; CBS College Publishing, New York (1986) 51-52

46. J.T. Marsh, *An Introduction to Textile Finishing*, Sixth (revised) Impression; Asia Publishing House, Mumbai (1957)

47. M. R. Julià, M. Cot, P. Erra, D. Jocić, and J. M. Canal, "The use of chitosan on hydrogen peroxide pretreated wool", *Textile Chemists and Colorists*, **30**(8), 78-83 (1998)

48. M.R.Julia, E.Pascual and P.Erra, "Influence of molecular mass of chitosan on shrink resistance and dyeing properties of chitosan treated wool", *Journal of Society of Dyers and Colourists*, **116**, Feb (2000) 62-66

49. M. R. Julià, D. Brunso, D. Jocić, and P. Erra, The use of chitosan on wool shrinkresistance, in *Advances in Chitin Science*, Vol. II, A. Domard, G.A.F. Roberts, and K.M. Vårum, Eds., Jacques André Publisher, Lyon, France (1997)

797-802

50. P. Erra, R. Molina, D. Jocic , M.R. Julia, A. Cuesta and J.M.D. Tascon, "Shrinkage properties of wool treated with low temperature plasma & chitosan biopolymer", *Textile Research Journal*, **69** (11) (1999) 811-815
51. Y.J. Jeong, S.Y.Cha, W.R.Yu and W.H.Park, "Changes in mechanical properties of chitosan treated wool fabric", *Textile Research Journal,* **72** (1) (2001) 70-76
52. A Abou-Okeil and O.A. Hakeim, "Effect of metal ion binding of chitosan on the printability of pretreated wool fabric", *Coloration Technology*, **121** (2005) 41-44
53. Aly Sayad Aly, "Utilization of chitosan citrate as crease resistant and antimicrobial finishing agent for cotton fabric", *Indian Journal of Fibre & Textile Research*, **29**, June (2004) 218-222
54. W. H. Park, K. Y. Lee, J. H. Choi, W. S. Ha, B. H. Chang, "Characterization of chitosantreated wool fabric. I. Antimicrobial and deodorant activities", *Journal of Korean Fiber Society*, **33**, (1996) 855-860
55. Seong-il Eom, "Using chitosan as an antistatic finish for polyester fabric", *AATCC Review*, **1**(3) (2001) 57-60
56. E.S. Abdel-Halim, F.A. Abdel-Mohdy, Salem S. Al-Deyab, Mohamed H. El-Newehy, "Chitosan and monochlorotriazinyl-cyclodextrin finishes improve antistatic properties of cotton/polyester blend and polyester fabrics", *Carbohydrate Polymers*, **82** (2010) 202–208
57. J.Z. Knaul, M.R. Kassai, B.V. Tam and K.A.M. Greber, "Characterization of deacetylated chitosan and chitosan molecular weight-review", *Canadian Journal of Chemicals*, **76**(11) (1998) 1699- 1706
58. P.S.Kalsi, "Ch.3, Infrared Spectroscopy" in *Spectroscopy of Organic Compounds*, Sixth Edition, New Age International Publisher, N.Dehli, India (2004) 59-164
59. A. Bayat, A.M.M. Sadeghi, M.R. Avadi, M. Amini, M. Rafiee-Tehrani, A. Shafiee, H.E. Junginger, "Synthesis of *N, N*-dimethyl *N*-ethyl Chitosan as a Carrier for Oral Delivery of Peptide Drugs", *Journal of Bioactive and Compatible Polymers*, **21,** (2006) 433-444
60. Ping Li, Ya-Ni Dai, Jun-Ping Zhang, Ai-Qin Wang and Qin Wei, "Chitosan–

Alginate Nanoparticles as a Novel Drug Delivery System for Nifedipine", *International journal of Biomedical science*, **4**(3) (2008) 221-228

61. M.R. Avadi, G.M. Amini, A. M. Sadegi, M. Irfan, M. Amini, M. R. Tehrani and A. Shafiee, "Synthesis and Characterization of *N*- Diethyl Methyl Chitosan", *Iranian Polymer Journal*, **13** (5) (2004) 431-436
62. Elisabete Curtia; Sergio Paulo Campana-Filho, "Viscosity Behavior of Chitosan and *N*,*N*,*N*-Trimethylchitosan Chloride Salts in Acid-Free Aqueous Solution", *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, **43** (2006) 555–572
63. E. Bobu, R. Nicu, M. Lupei, F. Ciolacu and J. Desbrières, "Synthesis And Characterization Of *N*-Alkyl Chitosan For Papermaking Applications", *Cellulose Chemical Technology*, **45** (9-10) (2011) 619-625
64. Asako Hirai, Hisashi Odani and Akio Nakajima, "Determination of degree of deacetylation of chitosan by ^{1}H NMR spectroscopy", *Polymer Bulletin*, **26**(1) (1991)87-94
65. W.L. Xu, J. Wu and C.L. Fu, "Synthesis of Chitosan Quaternary Ammonium Salts", *Chinese Chemical Letters*, **12** (12) (2001)1081-1084
66. Guanghua Liu, Jianqun Gan, Aimin Chen, Qian Liu, Xusheng Zhao, "Synthesis and characterization of an amphiphilic chitosan bearing octyl and methoxy polyethylene glycol groups", *Natural Science*, **2** (7) (2010) 707-712
67. V.R. Gowariker, N.V. Viswanathan and Y. Sreedhar, "Polymer Solutions" in *Polymer Science*, New Age International Publisher, N.Dehli, India (1986) 332-362
68. Dunkan J Shaw, "Rheology" in *Introduction to Colloid and Surface Chemistry*, Fourth Edition, Butterworth-Heinemann (Copyright © 1992, Elsevier Science Ltd.), Oxford, England (1992) 244-260
69. M. Terbojevich and R.A.A. Muzzarelli, "Chitosan" *Handbook of Hydrocolloids*, G.O.Phillips and P.A. Williams (Eds), Woodhead Publishing Ltd, Cambridge, England (2000) 367- 378
70. Kinzo Nagasawa, Yasuo Tohira, Yuko Inoue and Noriko Tanoura, "Reaction between carbohydrates and sulfuric acid: Part I. Depolymerization and

sulfation of polysaccharides by sulfuric acid", *Carbohydrate Research*, Volume **18**(1) (1971)95-102

71. M. Vårum Kjell, Marit W. Antohonsen, Hans Grasdalen and Olav Smidsrød, "Determination of the degree of *N*-acetylation and the distribution of *N*-acetyl groups in partially *N*-deacetylated chitins (chitosans) by high-field n. m. r. spectroscopy", *Carbohydrate Research*, **211** (1) April (1991)17-23
72. Dierk Knittel, Gisela Materne and Eckhard Schollmeyer, "Degradation of chitosan sizes", *Melliand English*, **87**(9) (2006) E 142-E144
73. Feng Tian , Yu Liu, Keao Hu, Binyuan Zhao, "The depolymerization mechanism of chitosan by hydrogen peroxide" *Journal of Materials Science*, **38** (2003) 4709 – 4712
74. F. Lee, W.K.Lee, M.Y. Maskat, R.M. Illias, S.A. Aziz, K. Kamarulzaman and H. Osman, "Partial depolymerization of chitosan with the aid of bromelain", *Pakistan Journal of Biological Sciences*, **8**(01) (2005) 73-77
75. Trzciński S, "Combined Degradation of Chitosans**",** *Polish Chitin Society*, Monograph XI (2006) 103-111
76. W.S. Choi, K.J. Ahn, D.W. Lee, M.W. Byun and H.J. Park, "Preparation of chitosan oligomers by irradiation", *Polymer Degradation and Stability*, **78**, (2002) 533-538
77. S. Baxter, S. Zivanovic and J. Weiss, "Molecular weight and degree of acetylation of high-intensity ultrasonicated chitosan", *Food Hydrocolloids*, **19** (2005) 821-830
78. K.V.Harish Prashant and R.N. Tharanathan, "Chitin/Chitosan: modifications and their unlimited application potential- an overview", *Trends in food Science & Technology*. **18** (2007) 117-131
79. N.N. Kabal'nova, K.Y. Murinov, R. Mullagaliev, N.N. Krasnogorskaya, V.V. Shereshovets, Y.B. Monakov and G.E. Zaikov, "Oxidative destruction of chitosan under effect of ozone and hydrogen peroxide", *Journal of Applied Polymer Science*, **81** (2001) 875-881
80. V.A. Demin, N.N. Kabal'nova, G.I. Osipova and V.V. Shereshovetz, "Depolymerization of cellulose upon ozonation" *Russian Journal of Applied*

Chemistry, **66** (1993) 2562

81. M. Yalpani and D. Pantaleone, "An examination of the usual susceptibilities of aminoglycans to enyamatic hydrolysis", *Carbohydrate Research*, **256** (1994) 159-175
82. A.V. Ilyina, V.E. Tikhonov, A.I. Albulov, V.P. Varlamov, "Enzymatic preparation of acid- free-water soluble chitosan", *Process Biochemistry*, **35** (2000) 563-568
83. Shirui Mao, Xintao Shuai, Florian Unger, Michael Simon, Dianzhou Bi and Thomas Kissel, "The depolymerization of chitosan: effects on physicochemical and biological properties", *International Journal of Pharmaceutics*, **281** (2004) 45–54
84. A .Tager, "Rheological properties of polymers in viscofluid state", in *Physical Chemistry of Polymers,* MIR Publishers- Moscow (1972) 241-272
85. R. Shephard, S. Reader and A. Falshaw, "Chitosan Functional Properties", *Glycoconjugate J,* **14** (1997) 535-42
86. Jae Kwan Hwang and Hae Hun Shin, " Rheological properties of chitosan solutions", *Korea-Australia Rheology Journal*, **12**(3/4), December (2000)175-179
87. M.L. Tsaih and R.H. Chen, "Effects of ionic strength and pH on the diffusion coefficients and conformation of chitosans molecule in solution", *Journal of Applied Polymer Science*, **73** (10) September (1999) 2041–2050
88. J.Y. Cho, M.C. Heuzey, A. Begin and P.J. Carreau, "Viscoelastic Properties of Chitosan Solutions: Effect of Concentration and Ionic Strength", *Journal of Food Engineering*, **74**(4) (2006) 500-515
89. N. Boucard, L. David, C. Rochas, A. Montembault, C. Viton, and A. Domard, "Polyelectrolyte microstructure in chitosan aqueous and alcohol solutions", *Biomacromolecules*, **8** (4) (April 2007) 1209–1217
90. Mayyas M.A. Al-Remawi, "Properties of Chitosan Nanoparticles Formed Using Sulfate Anions as Crosslinking Bridges", *American Journal of Applied Sciences*, **9**(7) (2012) 1091-1100
91. Xiao Ling , Yu Zu-yu , Yang Chao , Zhu Hua-yue and Du Yu-min, "Swelling Studies of Chitosan-Gelatin Films Cross-Linked by Sulfate", *Wuhan University*

Journal of Natural Sciences, **Vol. 9** No. 2 (2004) 247-251

92. Bhumkar D R & Pokharkar V B, "Studies on effect of pH on cross linking of chitosan with sodium tripolyphosphate: A Technical Note", *AAPS Pharm. Sci. Tech,* **7**(2) (2006) E1 – E6.
93. Cristóbal Lárez Velásquez, Joel Sánchez Albornoz & Enrique Millán Barrios, "Viscometric stidies of chitosan nitrate and chitosan chlorhydrate in acid free NaCl aq solution", e-*Polymers,* No.014 (2008)1-8
94. H. R. Cooper, "Yellowing of textiles due to atmospheric pollution", *Textile Progress,* (A special issue on Update on Yellowing), **15** (4) (1987) 1-6
95. T. Yui, K. Imada, K. Okuyama, Y. Obata, K. Suzuki and K. Ogawa, "Molecular and crystal structure of the anhydrous form of CS", *Macromolecules,* **27**(26) (1994) 7601-5
96. Bhuvana, Giri Dev, Raghunathan, Subramaniam, "Studies On Frictional Behaviour Of Chitosan coated Fabrics", *AUTEX Research Journal,* **6** (4) December (2006) 216-222
97. V.A.Shenai, Technology og Dyeing, Vol VI, 3rd Ed, Sevak Publishers, Mumbai, (1984)
98. E.R.Trotman, *Dyeing and Chemical Technology of Textile Fibres,* 6th edition, (1984) Pub. Charles Griffin and Co Ltd, London, England
99. Yuan Gao and Robin Cranston, "Recent Advances in Antimicrobial Treatments of Textiles", *Textile Research Journal,* **78**(1) (2008) 60–72
100. P. Bajaj, "Ecofriendly finishes for textiles", *Indian Journal of Fibre & Textile Research,* **26**, March-June (2001) 162-186
101. T.L. Vigo and M. A. Benjaminson, "Antimicrobial fiber treatments and disinfection", *Textile Research Journal,* July (1981) 454-462
102. Ian Holme, "Antimicrobial Imparts durable freshness", *International Dyer,* **187**(01) (2002) 9-11
103. Mukesh Kumar Singh., "21st century with deodorant fabrics", *Man Made Textiles In India,* **14** (7) (2002) 279-286
104. Yoshihiro Hasebe, Kazuo Kuwahara and Shinichi Tokunaga , *AATCC Review,* 1(11) (2001) 23-27.

"Chitosan hybrid deodorant agent for finishing textiles."

105. E.L .Schmidt and O.R.Ruschmeyer, "Cellulose Decomposition in Soil Burial Beds: I. Soil Properties in Relation to Cellulose Degradation", *Applied Microbiology*; **6**(2) Mar (1958)108–114
106. G.J. Tsai and W.H. Su, "Antibacterial activity of shrimp chitosan against Escherichia coli", *Journal of Food Protection*, **62**(3) (1999) 239-243
107. Chun Ho Kim and Kyu Suk Choi, "Synthesis and antibacterial activity of quaternized derivatives having different methylene spacers", *Journal of* Industrial *Engineering and Chemical*, **8**(1) (2002) 71-76
108. N.R. Sudarshan, D.G. Hoover and D. Knorr, "Antibacterial action of chitosan", *Food Biotechnology*, **6** (1992) 257- 272
109 X.F. Liu, Y.L. Guan, D.Z. Yang, Z. Li, and K.D. Yao, "Antibacterial action of chitosan and carboxymethylated chitosan", *J. Appl. Polym. Sci.*, **79**, (2001)1324-1335
110. R.G. Cuero, G. Osuji and A. Washington, "N-carboxymethyl chitosan inhibition of aflatoxin production: role of zinc", *Biotechnology Letters*, **13** (1991) 441-444

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF NANO-CHITOSAN DISPERSIONS AND THEIR APPLICATION ON COTTON FABRIC

3.1 INTRODUCTION

Preliminary experiments reported in chapter 2 shown that some of properties of the cotton fabric improved on application of chitosan on it. The dyeability of cotton fabric towards direct dyes was enhanced significantly due to chitosan pretreatment and the degree of improvement was found to be a function of molecular weight and concentration of chitosan. The fastness to washing of direct dye on chitosan pretreated fabric, however, was only slightly improved especially for the low molecular weight chitosan applications. But the post-dyeing chitosan treatment, in general, has improved the washing fastness of direct dyed cotton fabric. The moisture related properties were in tolerable limits. Chitosan treatment was found to impart resistance to microbial attack. The appearance and handle of the treated fabric, however, was severely affected and lost its natural 'cotton feel'. The wrinkle recovery property was found to be deteriorated. The very large molecular size and consequently high viscosity of chitosan restricts its penetration into the fibre and fabric structure and leads to only the surface deposition. The surface deposition of this high polymer affects the feel and appearance of the treated textiles. This may also leads to maximum accumulation of dye on surface thereby reducing the all round fastness properties especially washing, rubbing and light fastness. Today's need, however, is to improve above properties without altering the inherent natural qualities of cotton. It is possible by achieving the maximum penetration of polymer particles into fibre structure and increasing its effectiveness at low concentration. Penetration of chitosan solution can be improved by lowering the viscosity of its solution, which can be obtained by lowering the concentration and/or by reducing its particle size. Reduction in concentration of chitosan, however, decreases its effectiveness. An alternative way of improving its effectiveness is to drop down its particle size towards nano level. Reduction

---

Contents of this chapter is published in:
1) *Indian Journal of Fibre & Textile Research,* Vol. 38, March (2013) 14-21
2) *Research Journal of Engineering Sciences,* Vol. 1, No. 4, October (2012) 9-15

in particle size decreases viscosity, offers greater surface area and hence enhances the effectiveness of chitosan. This is the basic of 'nano technology'.

The concept of 'nanotechnology' lies in the fact that the properties of substances dramatically change when their size is scaled down to nanometer range. The first use of this concepts (but predating use of that name) was in "There's Plenty of Room at the Bottom," a talk given by a Nobel laureate physicist Richard P. Feynman at an American Physical Society meeting at Caltech on December 29, 1959. Feynman described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, so on down to the needed scale. The word nanotechnology, however, was used for the first time in 1974 by Prof. Norio Taniguchi of Tokyo Science University while explaining the Silicon machined down to the small particle-smaller than one micron. In 1986, K Eric Drexler wrote "Engines of Creation" and also introduced the term Nanotechnology. In general, "Nanotechnology is the engineering and fabrication of objects with size less than 100 nm. Below 100 nm the properties like melting point, hardness, catalytic activity and magnetic properties vary with size, otherwise these properties in other material are considered to be constant" or "Nanotechnology is concerned with developing the tools for characterizing and manipulating materials on nanoscale (1-100 nm) and exploiting these tools for the development of new products and processes" or "Nanotechnology is defined as the understanding, manipulation, and control of matter at the nanoscale (1-100 nm) , such that the physical, chemical, and biological properties of materials (individual atoms, molecules, and bulk matter) can be engineered, synthesized, or altered to develop the next generations of improved materials, devices, structures, and systems" [1-4]. A nanometer is one billionth of a meter, roughly the width of three or four atoms. The average human hair is about 25,000 nanometers wide. The magnitude of nano-size can be visualized on scale shown in Figure 3.1.

Nanotechnology basically deals with the individually arranging atoms or molecules in desired places to obtain a hybrid product with desired and diverse properties [5]. Fabrication of nano matrices can, broadly, be done by two approaches:

- **Top down approach:** The top-down approach involves the fabrication of components from larger materials

- **Bottom up approach:** An approach to building things by combining smaller components, as opposed to carving them out of larger ones (top down)

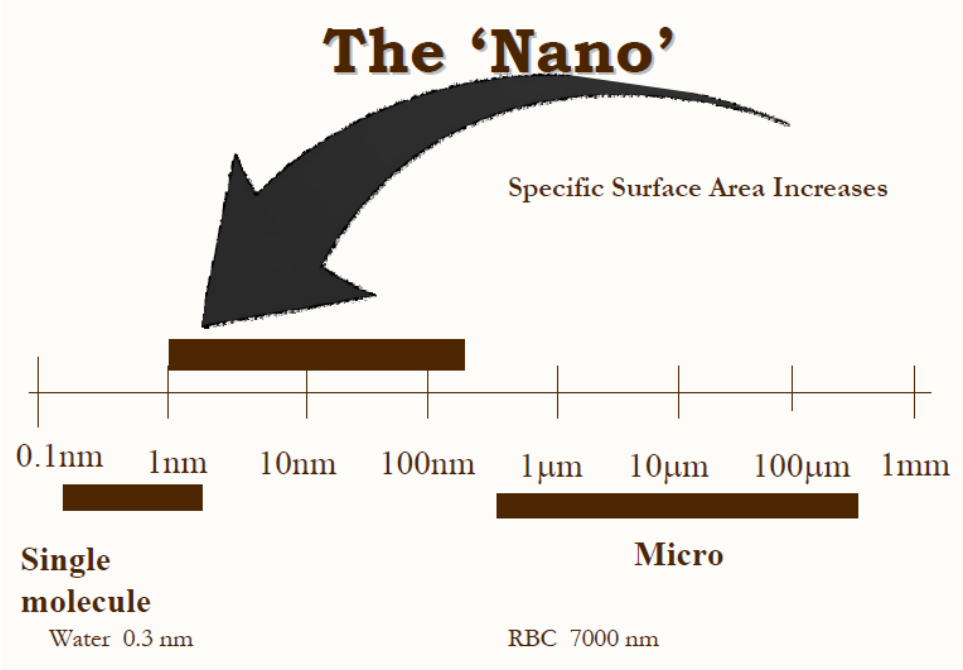


Figure 3.1 Nano size on scale

Nature follows the 'bottom up approach' rather than the 'top down approach' usually followed by humans to produce materials. The shapes are 'grown' rather than cut. All the living being can trace their origin to a single cell. Reduction in particle size to nanoscale can lead to changes in properties related to specific surface area, reactivity, quantum effects, strength, electrical characteristics, optical properties, magnetic behavior etc. As the particle size decreases, greater proportion of atoms are found at the surface compared to those in the 'body' [1, 5].

Nature has already developed polymeric nanoparticles with an elegant approach that combines chemistry and physics to create super-repellent hydrophobic surfaces. Lotus leaves are unusually water repellent and keep themselves spotless. The reason for this phenomenon is understood as the presence of nano sized bead like waxy structures on the surface of lotus leaf, which prevent water from wetting it. This phenomenon of water repellency in lotus leaves has actually inspired development of water repellant

nano-finish, which while conferring the water repellency to textile substrates allows the textile material to retain its natural handle and feel [6-8]. It has been demonstrated in recent years that the nanotechnology can be applied to textiles to enhance various properties, especially in functional coatings, such as fabric softness, durability and breathability, water repellency, fire retardency, antimicrobial properties, anticrease properties, U.V. protection, self cleaning properties and like in fibre, yarn and fabrics [2,6,7,9]. Undyable polypropylene fiber can be made dyeable by dispersing nanoclay, modified with quaternary ammonium salts, into polypropylene melt before spinning. After fiber formation the infused quaternary ammonium groups act as efficient dye sites [10]. A combined effect of wrinkle free and stain repellency can be obtained by treating fabric with 10nm tiny particles with both polar and non polar moieties imparting extremely low free surface energy. These nanoparticles cross link with cellulose to give the desired amount of wrinkle resistance. Such hybrid nanoparticles when incorporated with highly fluorinated silanes impart stain repellency. Nanotechnology can also be made applicable in the production of smart textiles. Application of carbon nano tubes can give rise to textile materials that have thermal and electrical conductivity sensible to touch and feel. Garments of such fabric can understand any abnormality in heart beat and then send a signal to family doctor or spouse [6, 11, 12]. The inorganic UV blockers are preferable to organic blockers as they are non-toxic and chemically stable under exposure to both high temperature and UV. Usually certain semiconductor oxides such as TiO_2, SiO_2, ZnO and Al_2O_3 are used as UV blockers. Rayleigh's scattering is dependent upon the wavelength where the scattering is inversely proportional to the wavelength to the fourth power. This theory predicts that in order to scatter UV radiation between 200 to 400 nm, the optimum particle size will be between 20 to 40 nm. UV blocking treatment for cotton fabric is given by using sol-gel method. A thin layer of titanium dioxide is formed on the surface of the treated fabric which provides excellent UV protection fast to washing [6, 13]. Nanosized silver, TiO2 and ZnO exhibit antimicrobial properties. Nanosilver is very reactive to protein when contacting with bacteria and fungus; it will adversely affect the cellular metabolism and inhibit the cell growth. Fabrics treated with nano TiO2 can provide effective protection against bacteria and discoloration of stain due to the photo catalysis effect of this agent. Nano ZnO provides effective photo catalytic properties once

it is illuminated by light and it is employed to impart antibacterial properties to textiles [14-18].

Chitosan is a biopolymer that has received much attention and has been extensively studied for micro- and nanoparticles preparation. It is possible, for a given molecular size chitosan, to reduce the particle size to nano level by 'bottom-up' approach as a result of a self assembling or cross linking processes in which the molecules arrange themselves into ordered nano scale structure either by physical or covalent inter- or intramolecular interactions. One of the trends in synthesis process is to pursue a nano scale emulsion, through which finishes can be applied to textile material in a more thorough, even and precise manner. Finishes can be emulsified into nano -micelles, made into nano-sols or wrapped in nano-capsules that can adhere to textile substrates more evenly. One popular method of nano fabrication of chitosan is gel ionization technique by reaction with polyanions such as sodium tripolyphosphate (TPP) [19-21]. The potential applications of nano chitosan are well demonstrated in medical field particularly as controlled drug delivery systems [22, 23]. However, their applications in textiles are not yet clearly investigated. The practical applications of such nano chitosan to textiles at shop floor level demands the consideration of establishment of suitable technology for the productions of nano chitosan dispersions, characterization and the stability of standing baths. Therefore an attempt, in the present chapter, is made to set a simple methodology to produce nano chitosan by ionotropic gelation with sodium tripolyphosphate (TPP). The samples were characterized by particle size analysis and their polydispersity indices (pdi). Effect of various parameters such as molecular weight & concentration of chitosan, concentrations of TPP on particle size were determined. Attempts were made to correlate the viscosity behaviour with particle size of chitosan.

The synthesized nano-chitosan was applied to cotton fabric and then various properties of the treated fabric like appearance, absorbency, stiffness, dyeing behaviour, wrinkle recovery, resistance to microbial attack etc were examined. The fabric samples were pretreated with normal and nano chitosan solutions by pad-dry cure technique. The surface morphology of the nano chitosan treated cotton fabric was examined by SEM analysis.

3.2 MATERIAL AND METHODS

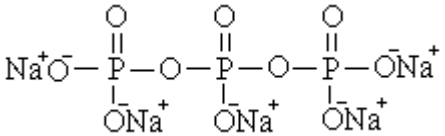
3.2.1 Fabric

The same fabric as specified in chapter 2, section 2.2.1 was used.

3.2.2 Dyes and chemicals

The details of various chemicals employed in present research investigation are given in Table 3.1.

Table 3.1 Specifications of various chemicals

Sr no	Name and Supplier	Specifications
1.	Pentasodium tripolyphosphate (TPP) (Qualikem Fine Chemicals Pvt Ltd, Vadodara, Gujarat)	Grade: Analytical  • Mol wt 367.86
2.	Silver sulphate (Qualikem Fine Chemicals Pvt Ltd, Vadodara, Gujarat)	Grade: Analytical $AgSO_4$ • Mol wt 311.8
3.	Sodium borohydride (Qualikem Fine Chemicals Pvt Ltd, Vadodara, Gujarat)	Grade: Analytical Chemical formula: $NaBH_4$ • Mol wt 37.83
4.	Trisodium citrate (Qualikem Fine Chemicals Pvt Ltd, Vadodara, Gujarat)	Grade: Analytical $Na_3C_6H_5O_7$ • Mol wt 258

Dyes namely C.I.Direct Red 81, C.I.Direct Blue 71, C.I. Acid Blue 158, Chitosan (CHT) and chemicals namely Chitosan (CHT), DMDHEU, acetic acid (CH_3COOH), sodium nitrite ($NaNO_2$), sodium acetate (anhydrous) (CH_3COONa), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium sulphate (Na_2SO_4) etc used were same as specified in chapter 2, section 2.2.1. Double distilled water was employed for all synthesis and analytical purposes.

3.2.3 Synthesis of low molecular weight chitosan

Low molecular weight chitosans were synthesized using same method described in chapter 2, section 2.2.4. Different grades of low molecular chitosan so prepared are listed in Table 3.3.

3.2.4 Synthesis of nano-chitosan and its characterization

Chitosan (CHT) stock solution (10 g/L) was prepared by dissolving CHT (1g) in 100 ml of acetic acid (10 g/L) solution and then filtered through filter fabric (mesh 128). Required amount of this solution (e.g. 10 ml) was taken in glass beaker, mixed with water (65 ml) and kept stirring on magnetic stirrer at about 400 rpm. TPP solution (5 g/L, 3ml) together with water (22 ml) was added drop wise to above stirring solution to give an opalescent nano chitosan dispersion corresponding to chitosan concentration 1 g/L. The sample was allowed to stand overnight and filtered through sintered glass filter of porosity grade G3 and preserved in refrigerator. The prepared nano-chitosan was nomenclatured as CHTN.

The particle size and size distribution of the chitosan were analyzed on the particle size analyzer (Zetasizer Nano ZS90, Malvern Instruments Ltd, UK). The test was performed at Chemical Engineering Department, Sardar Vallabhbhai National Institute of Technology, Surat.

3.2.5 Preparation of nano silver (Ag) colloid

Nano silver colloid was prepared using the method as discussed elsewhere [24]. In brief, a 100 ml solution of $1x10^{-3}$ M $AgSO_4$, kept in the specially designed reaction chamber, was slowly reduced by drop-wise addition of very dilute chilled solution (temperature ~2 ^{0}C) of sodium borohydride in a nitrogen atmosphere. During the process of reaction the solution mixture was stirred vigorously. When the colour of the solution turned to light yellow, 5 ml of 1 % trisodium citrate were added drop by drop with vigorous stirring.

3.2.6 Determination of viscosity

The viscosity and molecular weight of chitosan were determined as discussed in chapter 2, section 2.2.10.

3.2.7 Treatment of cotton fabric with nano-chitosan

Nano chitosan dispersion was applied onto fabric on a padding mangle (Model - PM0060388, R. B. Electronics & Engineering Pvt Ltd, Mumbai) with wet pick-up of

70% (Mangle Pressure: 20 psi, Speed: 3 m/min) by two dip- two nip method. After drying the fabric was cured in oven at 150 ^{0}C for 4 min. The sample was then washed in the following sequence**:** Hot wash (Twice) [85 ^{0}C/20 min] $\rightarrow$ Alkali wash [Soda ash 1 g/L, MLR 1:50] $\rightarrow$ Hot wash $\rightarrow$ cold wash $\rightarrow$Dry

3.2.8 Dyeing with direct dyes

Dyeing with direct dyes and the evaluation of colour depth (K/S) and fastness properties were done as described in chapter 2, section 2.2.7.

3.2.9 Scanning electron microscopy

Treated and untreated fabric samples were fixed on carbon coated aluminium sheets and then were observed under scanning electron microscope (Model JSM5610LV, version 1.0. Joel, Japan) in vacuum.

3.2.10 Determination of indices and stiffness of fabric

Determination of appearance indices and stiffness of fabric samples were done as described in chapter 2, sections 2.2.15 and 2.2.16 respectively.

3.2.11 Determination of tenacity

The tenacity and elongation of treated and untreated cotton fibres were measured on Stelometer described in chapter 2, section 2.2.9.

4.2.12 Determination of absorbency and crease recovery angle of fabric

Determination of absorbency and crease recovery angles of fabric samples were done as described in chapter 2, sections 2.2.17 and 2.2.18 respectively.

3.2.13 Soil burial test

The soil burial test fabric samples was carried out using the same method as described in chapter 2, section 2.2.19.

3.3 RESULTS AND DISCUSSION

3.3.1 Synthesis and characterization nano chitosan

Chitosan has fairly long linear structure with rigid conformation. These long molecules in solid state are, mostly, in the form of tightly folded random coils. Individual molecular coils are also not discrete and separate but are interpenetrating and entangled with each other. In solution, the solvent gradually diffuse into the polymer aggregates resulting into the swelling of the polymer. As swelling continues, the segments of the polymer are solvated and loosened out. The loosened polymer molecule then diffuses slowly out of the polymer phase and disperses in solvent phase, forming the solution. Since the molecules in a solid polymer remains entangled with neighbouring ones, polymer molecules during dissolution diffuse out as bunches of entangled molecules. Even when all chain segments of a polymer molecule in solution are unfolded and fully solvated, the molecules does not assume the shape of an extended straight chain but present in a coil form with the 'bound' solvent in the empty space between the unfolded segments. Such polymer coils along with 'bound', known as 'hydrodynamic' sphere or ellipsoid and the apparent volume is referred to as 'hydrodynamic volume'[25-27]. The overall dissolution process of chitosan acidic aqueous medium is schematically shown in Figure 3.2 and Figure 3.3.

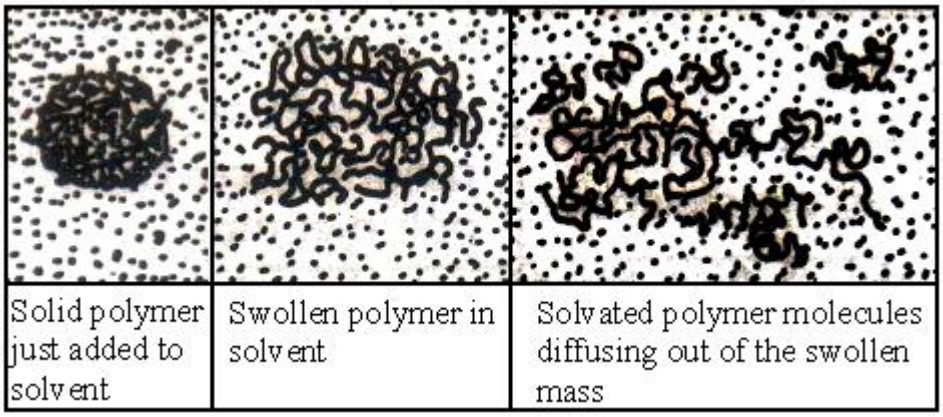


Figure 3.2 Dissolution of chitosan in acetic acid/water solvent

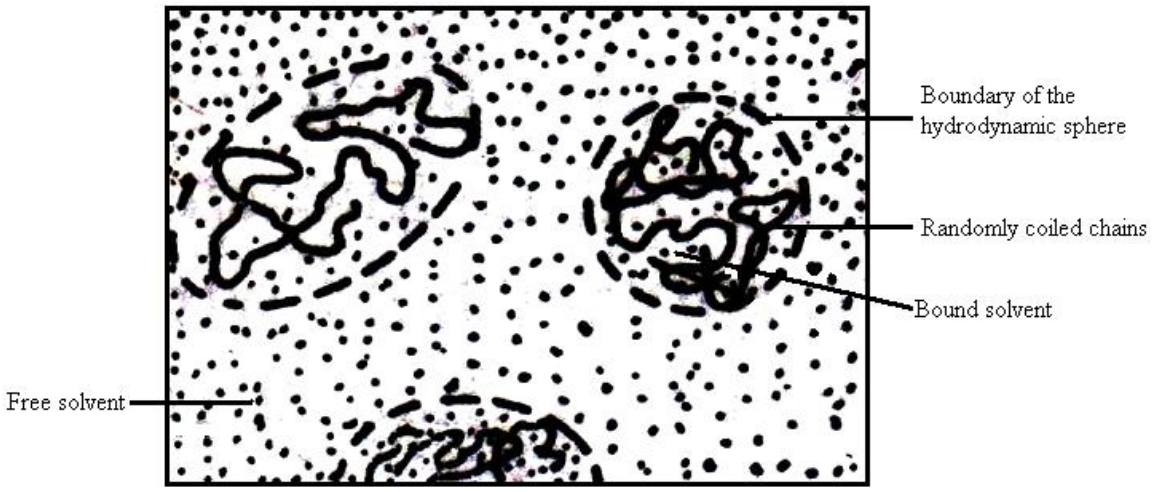


Figure 3.3 Hydrodynamic spheres of chitosan molecules in solution

The characteristic size of CHT hydrodynamic sphere, in our case, at 1 g/L concentration was determined to be 4014 nm. Such higher particle size offer higher viscosity to the solution confining the surface deposition of polymer film. The particle size of chitosan molecule can be scaled down by to nano level by 'bottom-up' approach as a result of a self assembling or cross linking processes [19]. To build materials by bottom-up approach, the first requirement is to have clusters of the material consisting of a few molecules. One such system of clusters of particles is the colloidal system. Colloids can be defined as: "a mixture with properties between those of a solution and fine suspension" [5]. Various method of synthesis of nano chitosan are described in literature [28, 29], which include precipitation or coagulation or desolvation method, covalent cross-linking, ionic cross-linking, emulsion droplet coalescence and reverse micellar method.

Drop wise addition of sodium sulfate into a solution of chitosan and polysorbate 80 (used as a stabilizer for the suspension) under both stirring and ultrasonication, desolvated chitosan in a particulate form. Although the investigators called the resulting suspensions micro spheres, the precipitated particles were at micro/nano interface (900±200 nm). Comparatively larger particle was attributed to their higher porosity observed by higher swelling ability [30, 31]. Dambies *et al.*[32] prepared chitosan particles using molybdate. It was observed a double layer structure corresponding to a very compact 100 μm thick external layer and an internal structure of small pores.

Emulsion-droplet coalescence method, introduced by Tokumitsu *et al.*[33], utilizes the principles of both emulsion cross-linking and precipitation. In this method, instead of cross-linking the stable droplets, precipitation is induced by allowing coalescence of chitosan droplets with sodium hydroxide droplets. A stable emulsion containing aqueous solution of chitosan along with the drug to be loaded is produced in liquid paraffin. Reverse micelles are thermodynamically stable liquid mixtures of water, oil, and surfactant. Microscopically, they are homogenous and isotropic structures consisting of aqueous-in-oil droplets separated by surfactant-rich films. Nano particles prepared by conventional emulsion polymerization methods are not only large (200 nm), but also possess a broad size range. Preparation of ultrafine polymeric nano particles with narrow size distribution could be achieved by using reverse micellar medium [34]. In this method, the surfactant is dissolved in an organic solvent to prepare reverse micelles. To this, aqueous solutions of chitosan and drug are added gradually with constant vortexing to avoid any turbidity. The aqueous phase is regulated in such a way as to keep the entire mixture in an optically transparent microemulsion phase. Additional amount of water may be added to obtain nano particles of large sizes. To this transparent solution, a cross-linking agent is added with constant stirring overnight. The self-assembly of chemically modified chitosan into nano particles can be employed through the fractional conjugation of polyethylene glycol, PEG, via an amide linkage and subsequent self-aggregation at basic pH [35-37]. Gong et al [38] reported a facile nonaqueous electrochemical approach to synthesizing different singlecrystal chitosan nanostructures on a stainless steel substrate, without using a template, catalyst, or surfactant. Chitosan was dispersed in propylene carbonate (PC) under mild ultrasonication and $LiClO_4$ was used as the supporting electrolyte during the electrochemical process.

Chitosan, by virtue of primary amino groups, under goes Schiff's base formation with aldehydes and ionic interactions with anionic compounds [39]. With the former property, chemically cross linked leading to a quite stable matrix of nano chitosan are obtained. Dialdehydes such as glutaraldehyde, salicylaldehyde etc are broadly used for cross linking the molecule in covalent formulations [19, 29, 40]. In the latter, chitosan hydrogels can be obtained by ionic gelation, where nano particles are formed by means of electrostatic interactions with polyanions such as pentasodium tripolyphosphate (TPP),

ethylene diamine tetra acetic acid (EDTA) etc. [23, 28, 41-43]. Owing to faster ionic reactions between chitosan and TPP, non toxic nature of these components [19] and ease of operation, the gel ionization technique for the synthesis of nano chitosan particles was adopted. From the physicochemical stand point, the interaction of chitosan with TPP is accepted to be mediated by the intramolecular crosslinking of tripolyphosphoric ($P_3O_{10}^{5-}$) ionic species, product of the dissociation of TPP in aqueous solution, with $-NH_3$ groups in chitosan. The intramolecular cross linking in chitosan molecule by gel ionization is schematically illustrated in Figure 3.4 and in Figure 3.5.

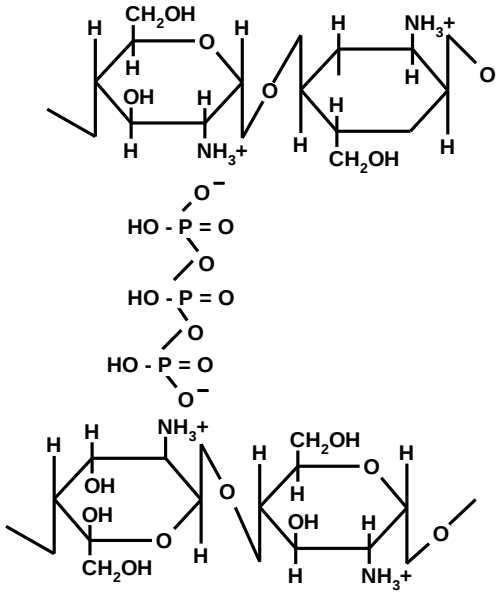
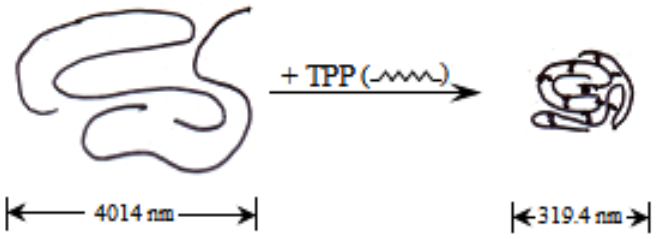


Figure 3.4 Chitosan-TPP complex formed as a result of ionic gelation



Chitosan- swollen molecule

Chitosan-TPP nano matrix

Figure 3.5 Schematic presentation of ionic gelation of chitosan with TPP

Stabilization of nano chitosan dispersion can be explained on the principle of Coulombic or electrostatic repulsion. Particles in a colloid, due to smaller size, are often pushed around by the molecular collisions of the surrounding media, an effect called Brownian motion. The Brownian motion is rather random, causing the particles to collide with each other frequently and aggregate to form larger particles, which settle down due to their weight. A prerequisite to utilization of colloids for nanotechnology is that they remain colloidally stable, i.e. they remain in suspension and resist settling down. This stability of a colloid can be achieved by means of electrostatic stabilization due to polycationic nature of chitosan in acidic medium and/or involving the creation of an electrical double layer arising from ions adsorbed on the surface of the particle and associated counter ions that surround the particle. Thus, if the electric potential associated with the double layer is sufficiently high, the Coulombic repulsion between the particles will prevent their agglomeration (Figure 3.6) [44]. The diffused solvent in nano gel exerts pressure on polymeric chain of loop, known as osmotic pressure. The osmotic pressure and intramolecular ionic repulsion tend to swell or enlarge the particle while the elastic contribution and the degree of cross linking act to shrink the gel. Thus from thermodynamics point of view, the stability or equilibrium of nano gel is attained when the forces responsible for swelling are balanced with the forces offering shrinkage [19].

Figure 3.6 Stability of nanoparticles due to electrostatic repulsion between the same ionic charges

A simple experimental set up designed for the synthesis of nano chitosan sols is shown in Figure 3.7. Chitosan solution was taken in a glass beaker and subjected to rapid stirring on a magnetic stirrer at ambient temperature (30 ^{o}C). TPP solution was then added drop wise from the separation funnel and continued stirring for 3 h, stored overnight and filtered through sintered glass filter of porosity grade G3 and preserved in

refrigerator. Amount of various ingredients taken for the synthesis of 100 ml of nano chitosan dispersion corresponding to 1 g/L concentration is enumerated in Table 3.2. The particle size distribution of above nanochitosan dispersions derived from varying molecular weight chitosans is shown in Figure 3.8 and their particle size is given in Table 3.3.

Table 3.2 Synthesis of CHTN

Ingredients	**Quantity, ml**
CHT (10 g/L)	10
Water	65
TPP (5 g/L)	3
Water	22
Total:	**100**

Conc of chitosan 1g/L, CHT:TPP=100:15, pH 4.3

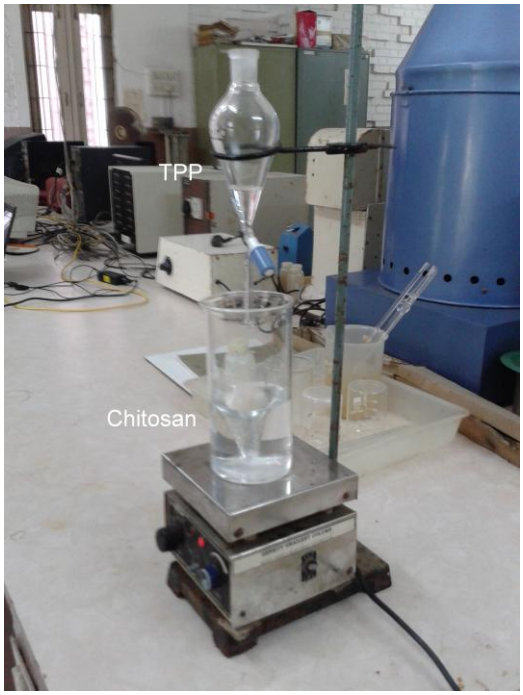
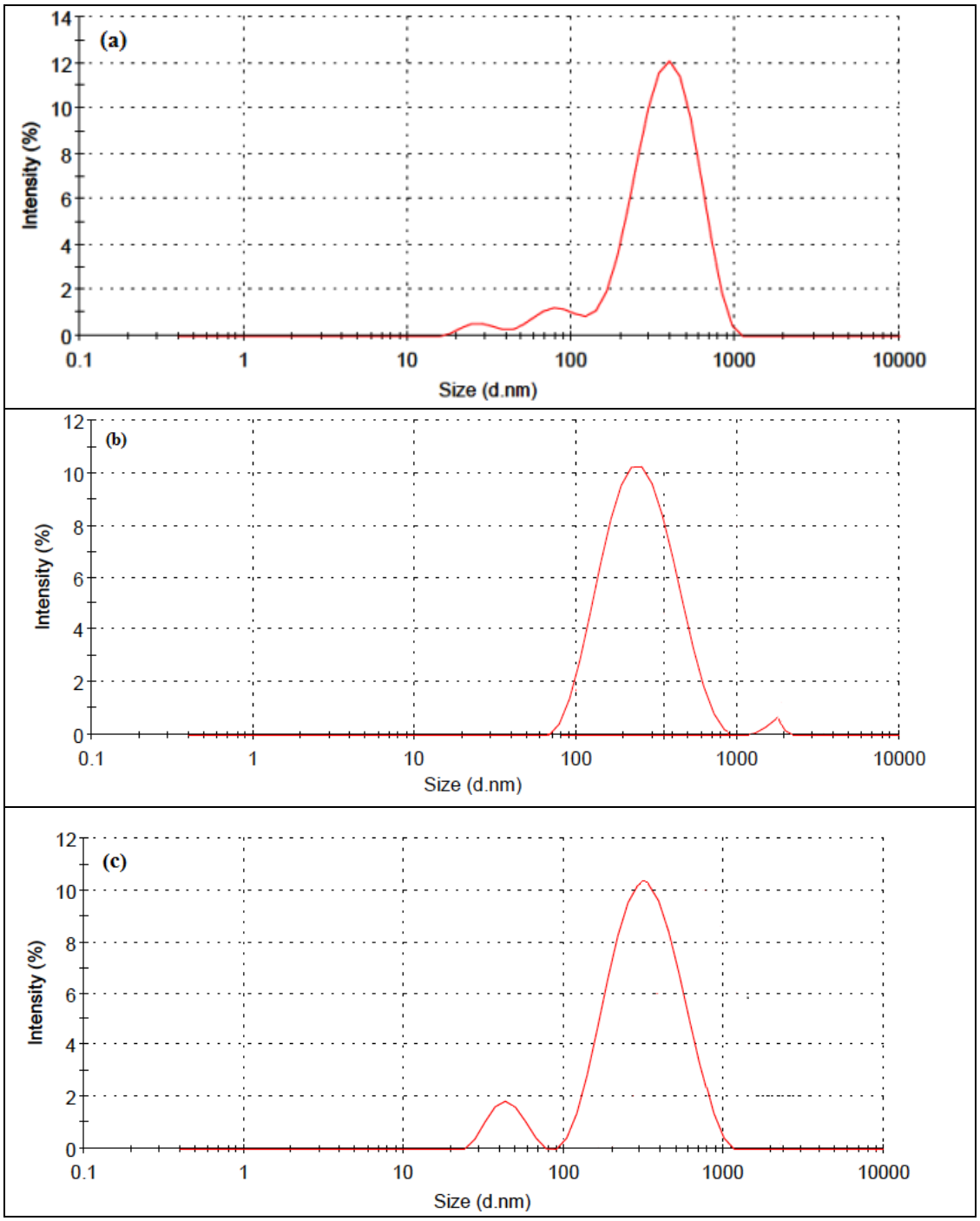


Figure 3.7 Experimental set up for the preparation of nano chitosan by ionic gelation method


(a)
Intensity (%)
Size (d.nm)
(b)
Intensity (%)
Size (d.nm)
(c)
Intensity (%)
Size (d.nm)

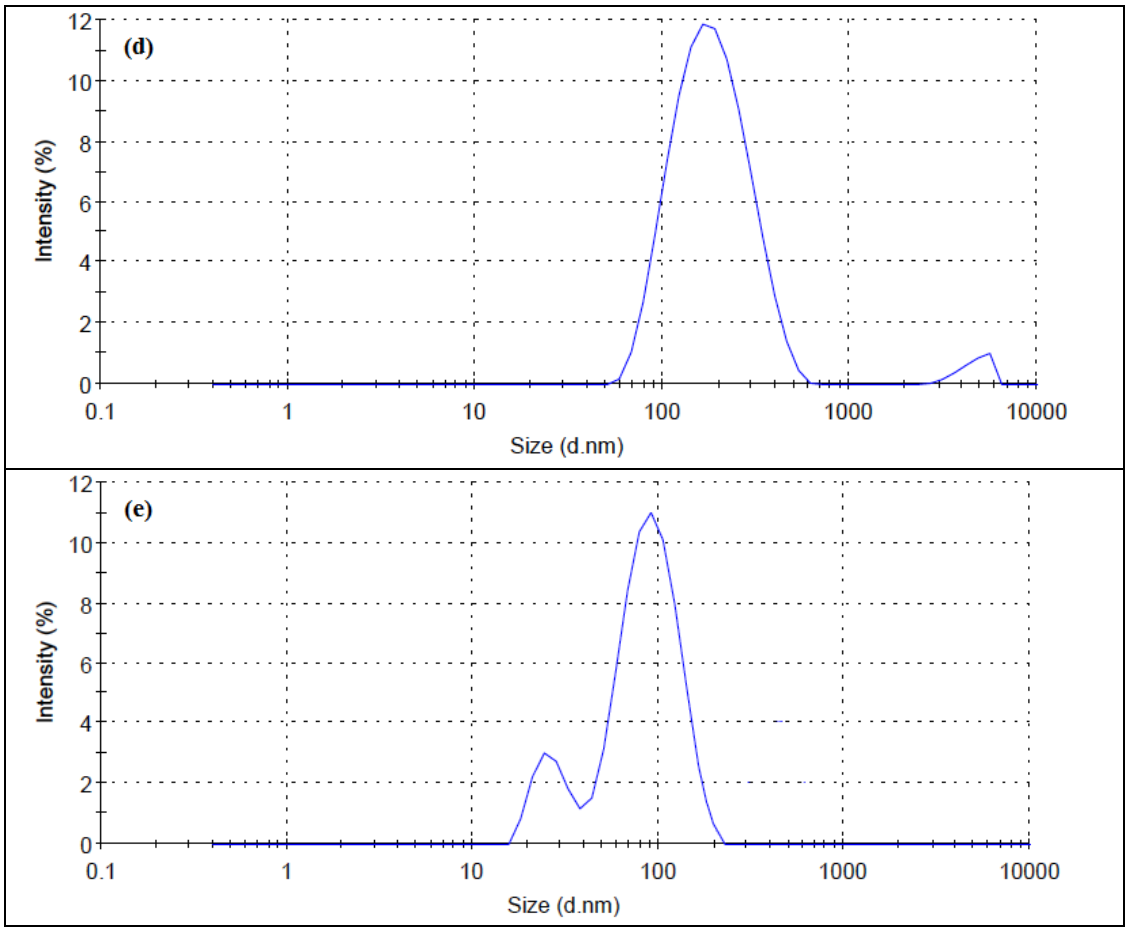


Figure 3.8 Size distribution of nano chitosan by intensity: (a) CHTN (319.4 nm) (b) CHT-D2N (271.6 nm) (c) CHT-D3N (231.1 nm) (d) CHT-D4N (195.2 nm) and (e) CHT-D5N (110.74 nm)

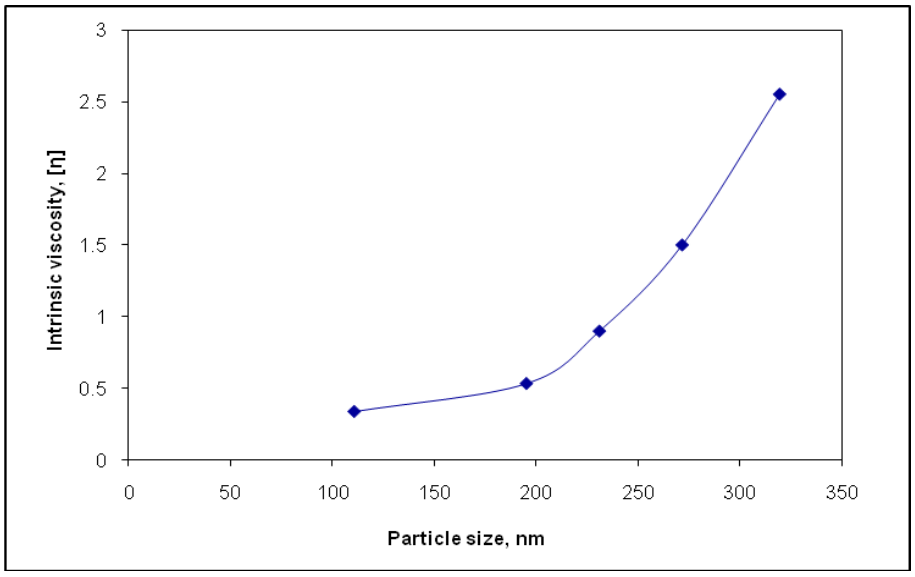
Table 3.3 Effect of molecular weight on particle size

Parent chitosan			**Synthesized nano chitosan**		
Sample code	**Intrinsic viscosity, [η]**	**Molecular weight, Mv**	**Sample code**	**Particle size, nm**	**Poly dispersity index (pdi)**
CHT	2.55	135,839	CHTN	319.4	0.422
CHT-D2	1.5	71,676	CHT-D2N	271.6	0.564
CHT-D3	0.9	38,733	CHT-D3N	231.1	0.466
CHT-D4	0.535	20,698	CHT-D4N	195.2	0.278
CHT-D5	0.34	11,986	CHT-D5N	110.74	0.467

Conc of chitosan 1g/L, CHT: TPP= 1:0.15

3.3.2 Effect of molecular weight of chitosan on particle size

Molecular weight of chitosan is an important property that determines the chain length and hence the hydrodynamic volume and therefore its influence on particle size of nano chitosan is expected. Various grades of low molecular weight chitosan can be produced by controlled depolymerization of high molecular weight one (namely CHT) by nitrous acid method as discussed in chapter 2. Very high molecular weight chitosans namely CHT-MC (Mol wt 654,127) and CHT-D1 (Mol wt 285, 231) were not chosen for the synthesis of nano particle due to their larger size. Chitosan (CHT) and its low molecular weight derivatives were employed for the synthesis nano chitosans in the present study.



Conc of chitosan 1g/L, CHT: TPP= 1:0.15

Figure 3.9 Particle size of chitosan as a function of intrinsic viscosity

The influence of molecular weight of chitosan on particle size is shown in Table 3.3 and the graphical correlation between intrinsic viscosity, a function of molecular weight, and particle size of nano chitosan is demonstrated in Figure 3.9. These data illustrate that, under a given condition of concentrations of CHT and TPP, with decrease in molecular weight, the particle size also decreased progressively and obeys a curvilinear relation. The tendency to form 'loop' is expected to be more favoured in larger chitosan chains than in shorter ones and can be expected to accommodate greater

amount of solvent to produce higher hydrodynamic volume [25, 45] and hence packed into relatively larger gelled nanoparticles and vise-versa. The large amount of bound solvent in nano gel derived from high molecular weight chitosan exerts higher osmotic pressure and the intramolecular ionic repulsion in acidic pH also contribute to larger size [19]. This relation of particle size with molecular weight in a definite condition of parameters may be useful for the preparation of nano chitosan of desired particle size. The regularity in particle size is determined by polydispersity index (pdi). Higher pdi value indicates the distribution in larger band width, multi population and varying degree of size. Almost similar levels of pdi value were observed (Table 3.3). A little deviation in values may be attributed to the molecular weight distribution of parent chitosan and depolymerization conditions.

3.3.3 Effect of concentration of chitosan on particle size

The effectiveness of nano chitosan on properties of treated cotton fabric is determined by its concentration in application bath. The concentration of chitosan in the formulation can be varied by two methods. Firstly, by the direct preparation method in which the dispersions of nano chitosan from CHT of different concentrations such as 0.25, 0.50, 1.0 g/L etc are prepared separately and secondly, by dilution method, where in a higher concentration nano chitosan dispersion (2 g/L) is prepared first and then diluted to desired concentration with rapid stirring (Table 3.4). The effects of these two methods and hence the concentration of starting material such as CHT for direct method and CHTN for dilution method respectively on particle size are presented in Figure 3.10 and in Table 3.5.

It was observed from above results that at higher concentration, in both the cases; the particle size of nano chitosan (CHTN) was comparatively larger and is progressively reduced with the lowering of concentration, nevertheless the molecular weight was same. The larger size of nano particles at higher concentration may be due to the aggregation of polymer molecules as a result of overlapping and also to the intermolecular cross linking through TPP bridging. On the other hand, as the concentration is lowered, the distribution of polymeric particle becomes more discrete and the intramolecular cross linkages in polymer molecule due to TPP bridging are likely to be favoured for lower particle size.

These results manifest that the poly dispersity indices (pdi) of directly prepared samples was comparatively lower and independent while for dilution method the values were higher and appeared to be dependent on the starting material. The particle size distribution curves, as illustrated in Figure 3.10, were broader for higher concentration samples and became narrow for lower concentration samples. Further, these bands were comparatively narrow for directly prepared samples indicating the uniform size distribution and are close agreement with their lower pdi values.

Table 3.4 Preparation of nano chitosan dispersions of varying concentrations

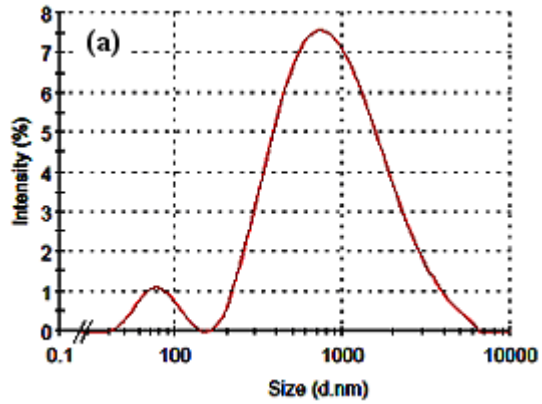
Method	**Ingredients**		**Quantity of ingredients (ml) for the preparation concentration grades, g/L:**				
			0.25	**0.50**	**1.00**	**1.50**	**2.00**
Direct method	Solution A	CHT (10 g/L)	2.5	5	10	15	20
		Water	72.5	70	65	60	55
	Solution B	TPP (5 g/L)	0.75	1.5	3.0	4.5	6
		Water	24.75	23.5	22	20.5	19
	Total (Solution A+B)		**100**	**100**	**100**	**100**	**100**
Dilution method	CHTN (2g/L)		12.5	25	50	75	100
	Water		87.5	75	50	25	-
	Total		**100**	**100**	**100**	**100**	**100**

Stock solutions: CHT (10g/L) was prepared in acetic acid (10 g/L) solution, TPP (5 g/L); CHT:TPP=100:15

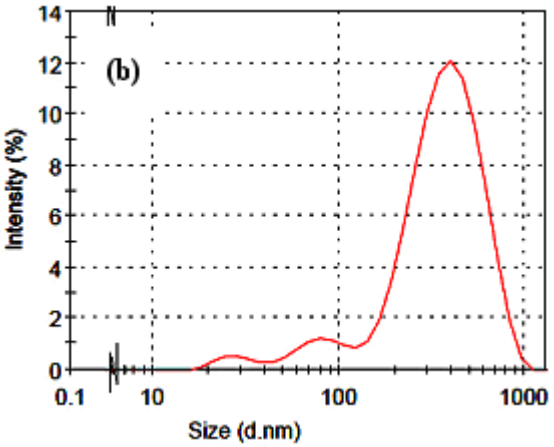
Table 3.5 Effect of preparation method and concentration of chitosan on particle size

Direct preparation method (Starting material: CHT, 10 g/L)				**Dilution method (Starting material: CHTN, 2 g/L)**			
CHT, g/L	**Particle size, nm**	**Poly dispersity index (pdi)**	**pH**	**CHTN, g/L**	**Particle size, nm**	**Poly dispersity index (pdi)**	**pH**
0.25	304	0.550	4.4	0.25	347.3	0.42	4.4
0.50	313.5	0.465	4.4	0.50	354.9	0.42	4.4
1.00	319.4	0.42	4.3	1.00	468.1	0.464	4.3
1.50	408.73	0.44	4.3	1.50	516.43	0.471	4.3
2.00	534.2	0.515	4.2	-	-	-	-

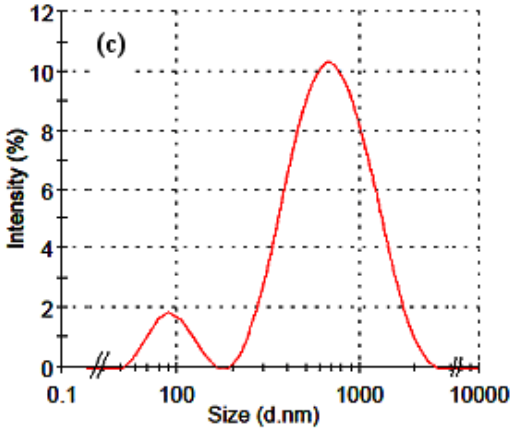
CHT1: TPP = 1:0.15



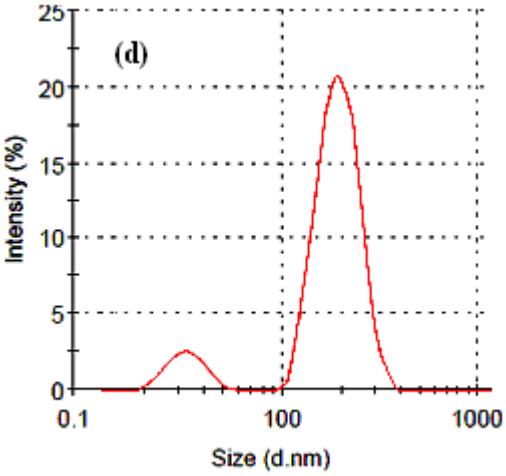
Direct method: 2g/L (534.2nm)



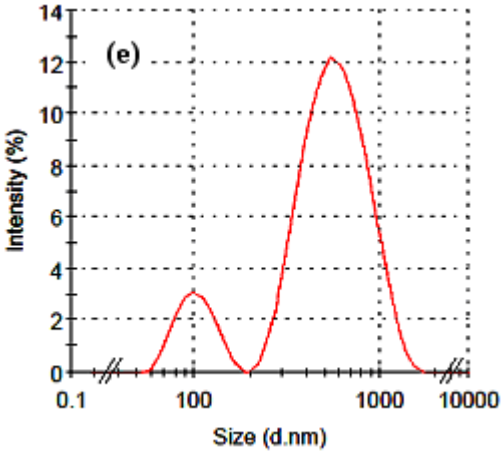
Direct method: 1g/L (319.4nm)



Dilution method: 1g/L (468.1 nm)



Direct method: 0.5g/L (313.5nm)



Dilution method: 0.5g/L (354.9 nm)

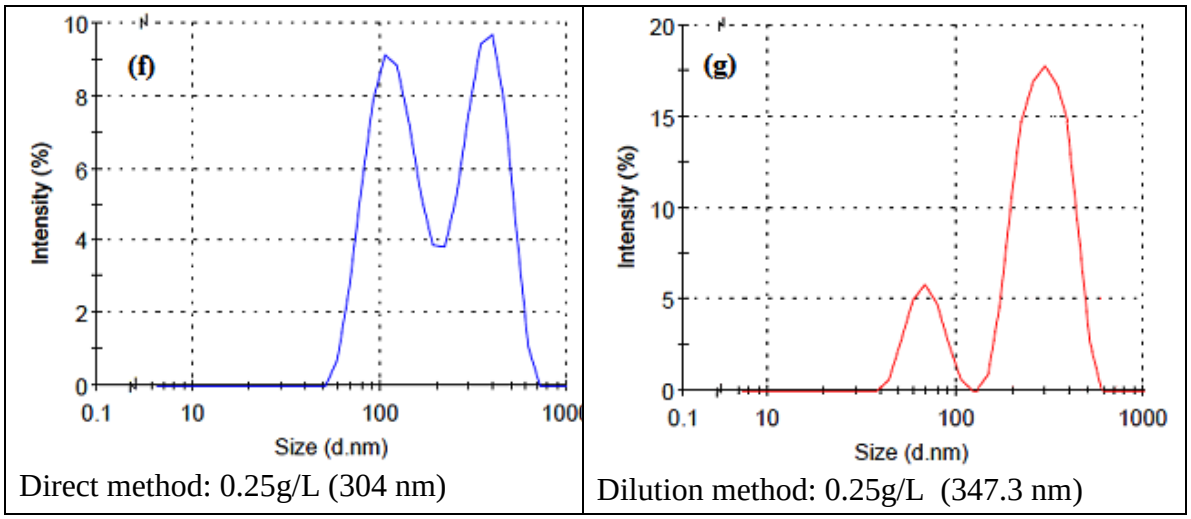
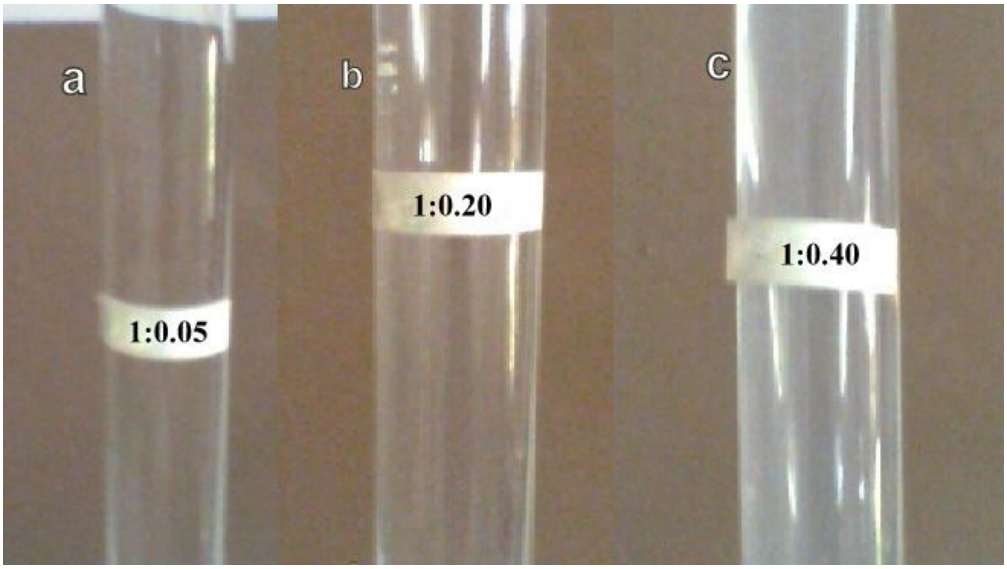


Figure 3.10 Particle size distribution of nano chitosan as a function of preparation methods

3.3.4 Effect of TPP concentration on particle size

In ionic gelation reaction, TPP a major ingredient for cross linking has a pronounced effect on the properties of CHTN dispersion. Therefore, the optimal amount of TPP concentration with respect to CHT concentration in formulation was investigated in detail. It was observed that with increase in the concentration of TPP the appearance of the system changed from clear viscous liquid to opalescent fluid and then precipitated (Figure 3.11). The effect of TPP concentration on the particle size is illustrated in Table 3.6 and in Figure 3.12.

At concentration of TPP below 0.05 g, very few phosphate ions were present to produce effective ionic linkages with chitosan amino groups; hence, the solution was clear. As the concentration of TPP was increased gradually, the solution became opalescent indicating the formation of nano chitosan. It was revealed from the same figure that with increase in concentration of TPP, the particle size of CHT-TPP nanomatrix decreased, reached to minimum at TPP concentration of about 0.15 to 0.25 g and then increased. Concentration of TPP above 0.30 g resulted precipitation. The precipitation at excessively higher concentration of TPP may be attributed to the aggregation of chitosan molecules due to excessive cross linking through TPP bridging. Similar trend in terms of viscosity was noticed when the relative viscosity was plotted against TPP concentration, Figure 3.13.



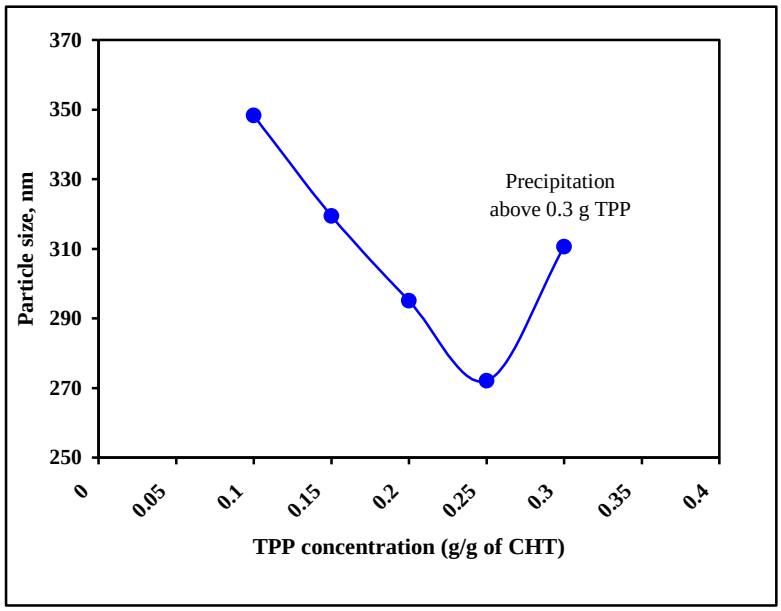
Conc of chitosan 1g/L

Figure 3.11 Effect of TPP concentration on appearance CHTN dispersion

Table 3.6 Effect of TPP concentration on particle size of nano chitosan

CHT:TPP	Ingredients, ml				Viscosity		Particle size, nm
	CHT	TPP	Water	Total volume	Flow time (T), sec	Relative viscosity (η_{rel})	
1:00	10	-	90	100	51.85	3.328	4014
1:0.05	10	1	89	100	46.86	3.010	-
1:0.10	10	2	88	100	39.04	2.507	348.3
1:0.15	10	3	87	100	32.25	2.071	319.4
1:0.20	10	4	86	100	27.16	1.745	295.1
1:0.25	10	5	85	100	23.12	1.485	272.06
1:0.30	10	6	84	100	30.13	1.935	310.6
1:0.35	10	7	83	100	16.91	1.086	ppt
1:0.40	10	8	82	100	16.28	1.045	ppt

Stock solutions: CHT (10 g/L) prepared in acetic acid solution 10 g/L, TPP (5 g/L);
Conc of nano-chitosan 1g/L, T_0 (Water) 15.57 sec, Temp 30 ^0C



Conc of chitosan 1g/L, Size of CHT molecular sphere in absence of TPP was 4014 nm

Figure 3.12 Effect of TPP concentration on particle size of CHTN

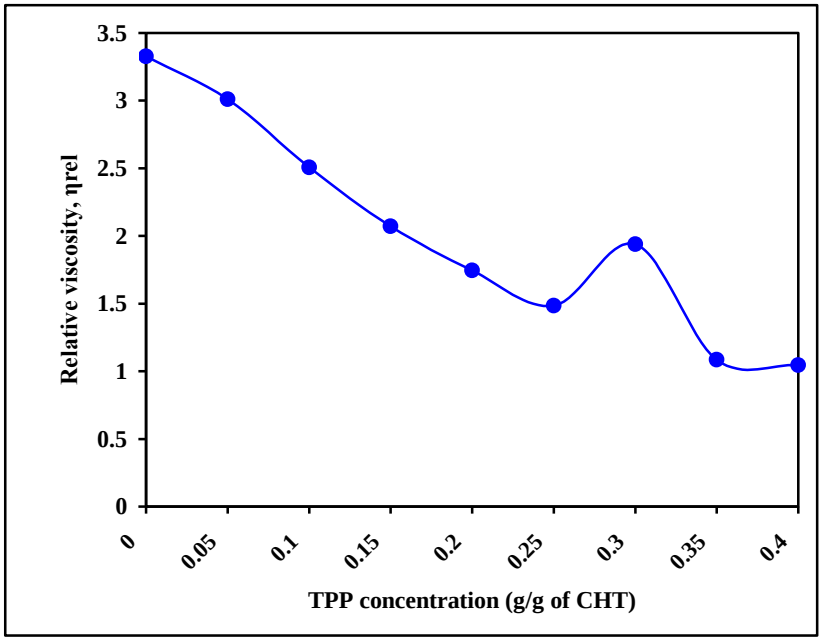


Figure 3.13 Relative viscosity of CHTN dispersion as a function of TPP concentration

3.3.5 Viscosity behaviour of nano chitosan dispersion

The viscosity of polymer solution, at the molecular level, is a direct measure of the hydrodynamic volume of the polymer molecules which in turn is governed by the

molecular size or the chain length and hence the molecular weight [26]. A correlation of molecular weight of chitosan with the particle size of respective synthesized nano chitosan is elucidated in section 3.3.2. The particle size of nano chitosan is also expected to influence the viscosity behaviour of its dispersion, which is presented in Table 3.7. The extent to which a parent chitosan scales down to nano level at a given concentration of CHT and TPP was also examined by comparing the relative viscosity of nano chitosan dispersion with that of respective parent chitosan solution as demonstrated in same table and graphically in Figure 3.14.

Table 3.7 Viscosity of nano chitosan dispersion as a function of particle size

Parent chitosan solution				**Nano chitosan dispersion**				
Sample code	**Molecular weight (Mv)**	**Flow time (T), Sec**	**Relative viscosity (η_{rel})**	**Sample code**	**Flow time (T), Sec**	**Relative viscosity (η_{rel})**	**Drop in viscosity on nano conversion, %**	**Particle size, nm**
CHT	135,839	51.81	3.33	CHTN	32.25	2.07	37.76	319.4
CHT-D2	71,676	28.57	1.84	CHT-D2N	22.80	1.46	20.26	271.6
CHT-D3	38,733	20.03	1.29	CHT-D3N	17.74	1.14	11.43	231.0
CHT-D4	20,698	17.77	1.14	CHT-D4N	16.38	1.05	7.76	195.2
CHT-D5	11,986	16.43	1.06	CHT-D5N	16.13	1.04	1.77	110.7

Conc of chitosan 1 g/L, CHT:TPP=1:0.15, T_0 (Water)= 15.57 sec, Temp 30 ^oC

It can be seen from Table 3.7 that the viscosity of CHTN dispersion decreased with reduction in particle size. However, the effect was more significant for larger particles than the smaller one. Obviously, the larger the particle size the higher will be the resistance offered for the flow of liquid and hence the higher will be the viscosity and vise versa. Comparatively slower fall in viscosity for small CHTN particles may be attributed to the low molecular weights of parent chitosan. It can be observed from Figure 3.14 that the percentage drop in viscosity from molecular (CHT) solution to corresponding nano chitosan (CHTN) dispersion follows a straight line. It means higher molecular weight chitosan scales down to nano size to greater extent than the lower molecular weight chitosan. This can be explained as follows; large size chitosan molecules in solution accommodate comparatively more amount of solvent and occupy

large ‘hydrodynamic’ volume. These swollen molecules compress to greater extent by ionotropic intramolecular cross linking with TPP by displacing the solvent, as demonstrated in Figure 3.5. On the other hand, the extent of swelling of low molecular weight chitosan is comparatively less [27] and hence lesser will be its tendency to compress.

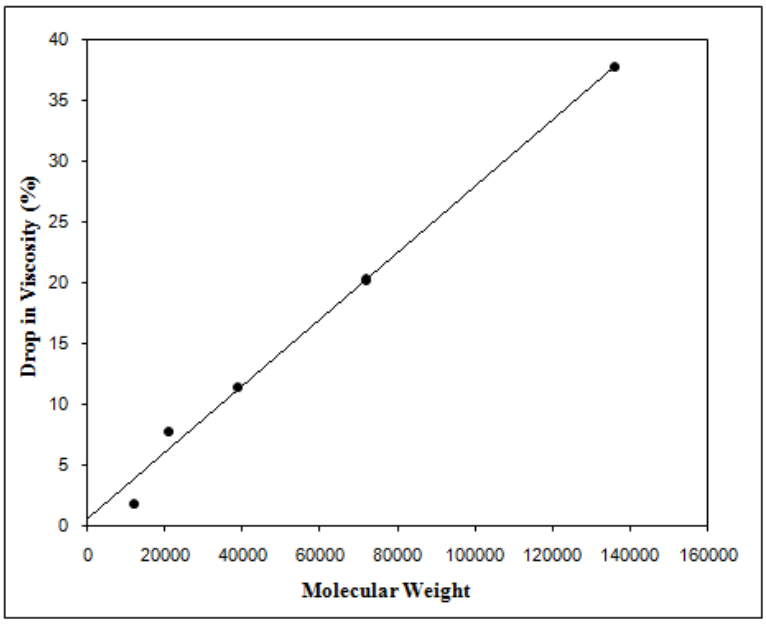


Figure 3.14 Drop in viscosity from parent to nano chitosan solution as a function of molecular weight

The biodegradability of chitosan is anticipated to be influenced by its particle size. Therefore the stability behaviour of standing baths of nano chitosan dispersion should be taken into consideration during its applications particularly to textile fabrics. The stability of nano chitosan dispersions for 24 h were analysed by viscosity measurements as shown in Table 3.8. It was observed that the change in viscosity of parent chitosan solution was governed by its molecular weight, which improved with decrease in weight. The stability behaviour of nano chitosan dispersion, on the other hand, was found to be different from that of parent chitosan solutions. The loss in viscosity of high molecular weight parent chitosan solution was somewhat higher than that of corresponding/respective synthesized nano chitosan dispersions. The integrity of nano chitosan i.e. small particle size was found to lose which were obtained from low molecular weight chitosans. The viscosity changes for most of the nano chitosan

dispersions in 24 h storage were tolerable and can be safely employed for applications. Complete biodegradation of nano chitosan dispersion, in general, was resulted in 3-4 days showing the formation of white globules as shown in Figure 3.15. Such spontaneous disintegration takes place under very mild conditions. The viscosity of parent chitosan solution sustained for longer time after initial loss in viscosity, chapter 2. This suggests that chitosan-TPP nanogels behave as metastable system and must be used fresh or must be stored lyophilized and fresh aqueous solutions only prepared when required [19]. Viscosity analysis and visual observations, therefore, may be the useful tools for stability inspections.

Table 3.8 Stability of nano chitosan solution as a function of particle size

Parent chitosan solution					**Nano chitosan dispersion**				
Sample Code	**Mol Wt (Mv)**	**Relative viscosity(η_{rel})**		**Drop in viscosity (%) after 24 h**	**Sample Code**	**Particle size, nm**	**Relative viscosity (η_{rel})**		**Drop in viscosity (%) after 24 h**
		Initial	**After 24 h**				**Initial**	**After 24 h**	
CHT	135,839	3.33	2.98	10.27	CHTN	319.4	2.07	2.00	3.68
CHT-D2	71,676	1.84	1.76	4.1	CHT-D2N	271.6	1.46	1.45	1.05
CHT-D3	38,733	1.28	1.25	2.6	CHT-D3N	231.0	1.14	1.13	1.18
CHT-D4	20,698	1.10	1.08	2.15	CHT-D4N	195.2	1.05	1.01	3.6
CHT-D5	11,986	1.05	1.04	1.73	CHT-D5N	110.74	1.04	1.01	2.27

Conc of chitosan 1 g/L, CHT:TPP=1:0.15, T_0 (Water)= 15.57 sec, Temp 30 ^oC

Figure 3.15 Stability study: white globular residue formed by microbial attack on CHTN

3.3.6 Effect of nano chitosan treatment on cotton fabric

Chitosan and nano chitosan solutions were applied onto fabric by conventional pad-dry cure technique. Having understood from chapter 2 that the progressive changes in performance in various properties of chitosan treatment at various concentrations, only a representative concentration of 1 g/L was chosen.

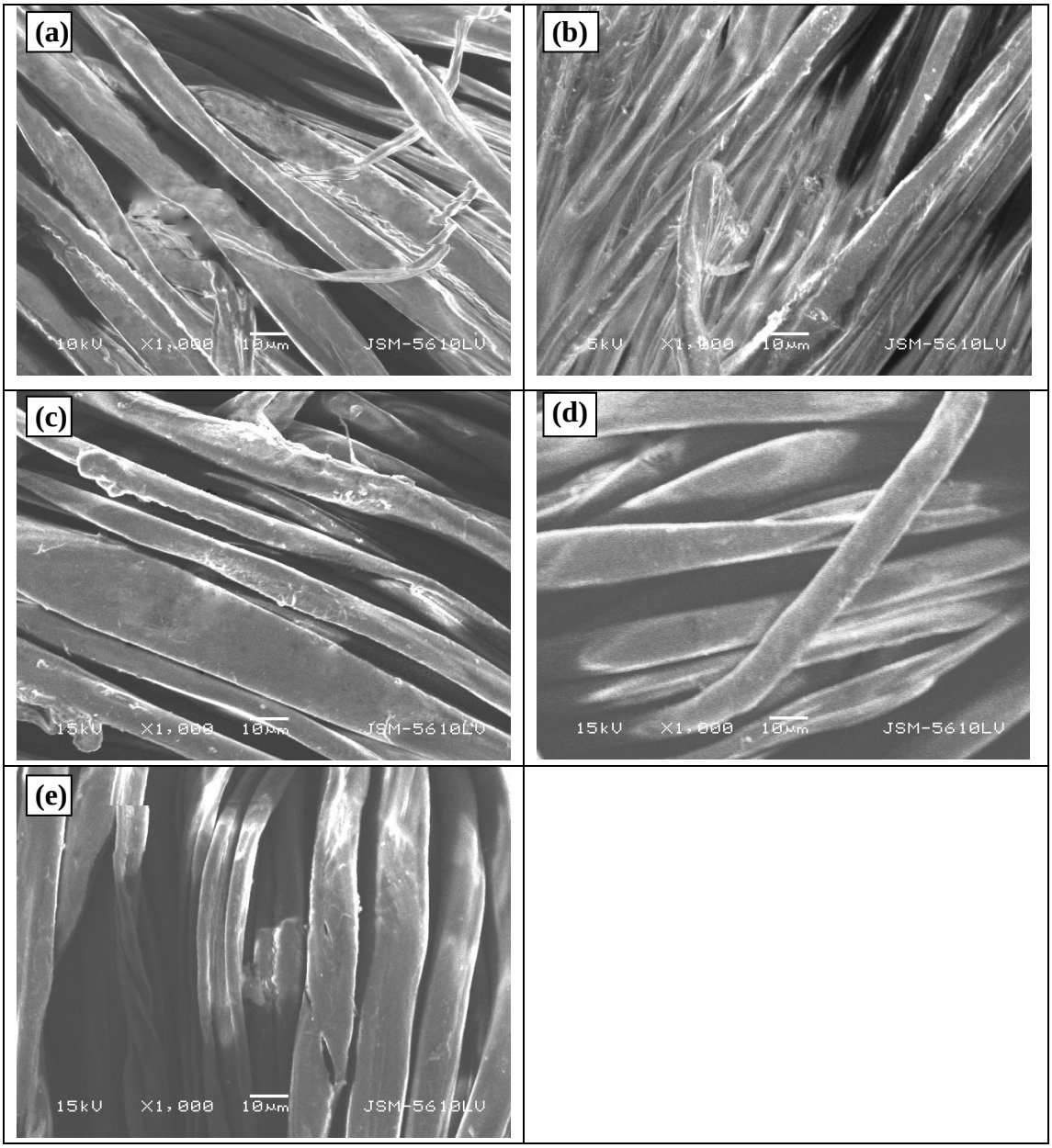


Figure 3.16 Scanning electron micrographs (x1000) of (a) control cotton fibre, (b) CHT treated fibres, (c) CHTN (319.4 nm) treated cotton fibres, (d) CHT-D4N (195.2 nm) treated cotton fibres and (e) CHT-D5N (110.7 nm) treated cotton fibres

The surface morphology of treated and untreated cotton was studied under scanning electron microscope, which is presented in Figure 3.16. Chitosan exhibits an inherent property of film formation, which is clearly seen as gloss on fibre surface as shown in figure SEM (b). Nano chitosan treated samples showed a different look in its microphotographs, which are presented in Figures 3.16(c, d and e).The appearance was non glossy and somewhat swollen. This effect became more significant when the particle size was reduced. It indicates a greater extent of penetration into the fibre structure rather than a surface deposition as film.

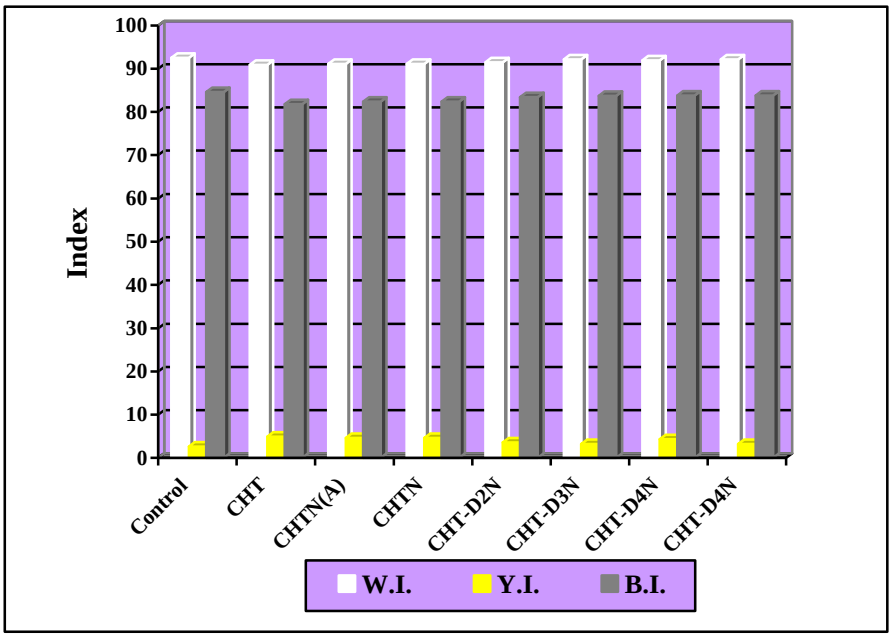
3.3.7 Effect of nano chitosan treatment on appearance and feel of cotton fabric

The appearance and the fabric feel are quite satisfactory. The results are illustrated in Table 3.9 and Figure 3.17. It was envisaged that the whiteness improved with reduction in particle size and reached well nearer to that of control sample. This may be attributed to the greater extent of penetration of nano-chitosan particles into fibre structure and allowing the cuticle for exposure. Deposition of normal chitosan, however, is confined to surface as a film, which alter the whiteness to some extent. This film may also impart stiffness to the fibre, where as a nano chitosan shows a little influence, as can be observed in same table.

Table 3.9 Effect of particle size of nano chitosan on appearance and stiffness of cotton fabric

Sample code	Particle size, nm	Appearance			Bending Length, cm	
		W.I.	Y.I.	B.I.	Warp	Weft
Control	-	92.5	2.6	84.6	2.05	1.68
CHT	4014	90.9	4.9	81.8	2.44	1.70
CHTN(A)	468.1	91.1	4.6	82.4	2.29	1.71
CHTN	319.4	91.1	4.6	82.3	2.26	1.70
CHT-D2N	271.6	91.5	3.6	83.4	2.24	1.70
CHT-D3N	231.0	92.1	3.2	83.7	2.24	1.71
CHT-D4N	195.2	91.9	3.4	83.8	2.21	1.70
CHT-D5N	110.7	92.1	3.2	83.8	2.19	1.70

Conc of chitosan derivatives in pad liquor 1g/L, CHTN (A) was obtained from nano CHT (2 g/L) by dilution method



Conc of chitosan derivatives in pad liquor 1g/L, CHTN (A) was obtained from nano CHT (2 g/L) by dilution method

Figure 3.17 Effect of particle size of nano chitosan on appearance of treated cotton fabric

3.3.8 Effect of nano chitosan on tensile properties of cotton fabric

During wet processing operations textile fabric is subjected to various chemical and thermal treatments. These treatments affect various properties of the fabric. The effect of nano chitosan on tensile properties such as tenacity and elongation at break are presented in Table 3.10. It is observed that there is reasonable reduction in fibre strength of normal chitosan treated fabrics. This drop in strength seems to be arised from the acid hydrolysis and/or thermal treatments and not due to chitosan, which is obviously envisaged from the strength of the blank treated sample. While, normal chitosans of different molecular weights show somewhat higher strength than that of the blank treated sample, nevertheless lower than the untreated one. The elongation property was not altered much when compared to blank sample. The nano chitosan treatment on the other hand showed improvement in fibre strength which further increased with the reduction in particle size. The elongation property, however, was slightly affected with the scaling down of particle size. Normal chitosan mostly confines its film deposition on fibre surface only and thus contribute to very small extent in load bearing phenomenon rather

may affect its symmetrical distribution of load. The improvement in fibre strength may be attributed to greater penetration of small particles and crosslink the adjacent fibre molecules by various forces between amino ($-NH_2$) and hydroxyl (-OH) groups of chitosan and hydroxyl (-OH) groups of cellulose molecules. The smaller the particle size, higher will be the surface area and hence the higher will be the cross links. The formation of *in-situ* three dimensional networks probably resists the adjacent fibre molecules to slip and lowers the elongation at break.

Table 3.10 Effect of nano chitosan treatment on tensile properties of cotton fabric

Parent chitosan treated fibres			**Nano chitosan treated fibre**		
Sample code	**Tenacity, g/tex**	**Elongation at break, %**	**Sample code**	**Tenacity, g/tex**	**Elongation at break, %**
Untreated cotton fabric	23.33	5.25	Untreated cotton fabric	23.33	5.25
Control	20.87	4.75	Control	20.87	4.75
CHT	20.48	4.75	CHTN-A	23.48	4.5
			CHTN	25.17	4
CHT-D2	21.01	4.5	CHT-D2N	25.62	4
CHT-D3	21.45	4.5	CHT-D3N	25.56	4
CHT-D4	22.19	4.25	CHT-D4N	25.71	3.75
CHT-D5	21.81	4.5	CHT-D5N	25.72	3.5

Conc of chitosan derivatives in pad liquor 1g/L, CHTN-A was obtained from nano CHT (2 g/L) by dilution method, Control: Blank treatment was given with acetic acid (10 g/L) by pad-dry cure method

3.3.9 Effect of nano chitosan treatment on absorbency of cotton fabric

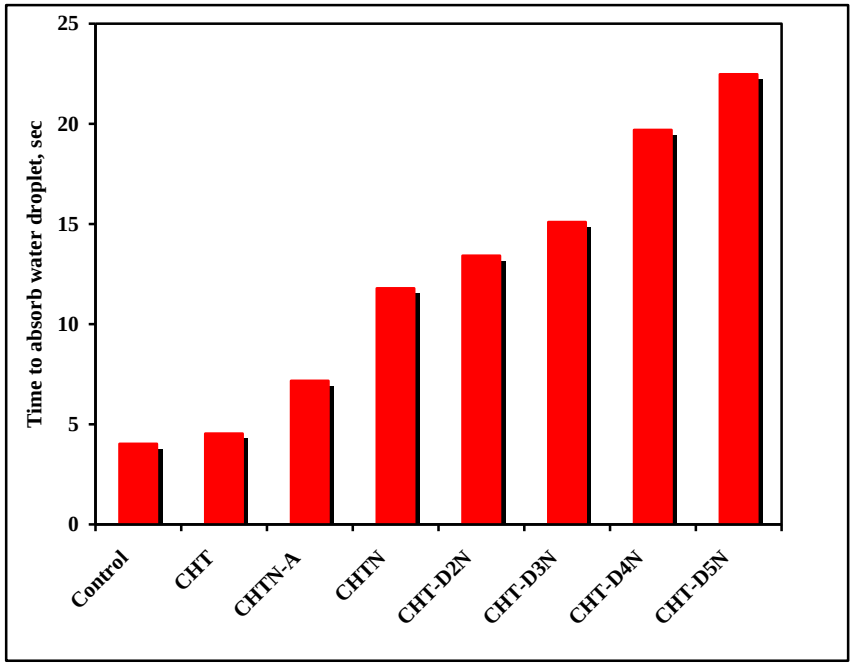
The absorbency, measured by drop penetration method, of nano chitosan treated cotton fabric was evaluated and shown in Table 3.11 and graphically in Figure 3.18. The absorbency was found to be decreased with the reduction in particle size. This may be elucidated by the example of lotus leaf effect. Distribution of nano chitosan particles as a thin layer over and beneath the surface, illustrated in Figure 3.16 (c, d and e), may roll out the water droplets. Nevertheless, the absorbency of nano chitosan treated samples is still within the tolerable limits of conventional wet processing conditions since this rise in water drop penetration time is due to the initial resistance offered by nano chitosan

particles and not due to any hydrophobic or water repellant hydrocarbon or silicone type films.

Table 3.11 Effect of particle size of nano chitosan on absorbency of treated cotton fabric

Sample code	Particle size, nm	Absorbency, sec						
		Readings						Average
Control	-	3.88	3.88	3.24	4.95	4.41	3.78	4.0
CHT	4014	4.28	3.95	4.62	5.12	4.46	4.81	4.5
CHTN-A	468.1	8.03	5.47	8.14	4.95	7.21	9.22	7.2
CHTN	319.4	10.98	11.52	11.92	12.36	9.81	14.15	11.8
CHT-D2N	271.6	13.45	13.68	12.69	15.08	13.36	12.26	13.4
CHT-D3N	231.0	14.81	15.12	16.71	12.61	17.43	13.86	15.1
CHT-D4N	195.2	20.36	19.52	22.81	18.08	23.01	14.36	19.7
CHT-D5N	110.74	22.51	18.71	26.08	22.32	21.42	23.78	22.5

Conc of chitosan derivative in pad liquor 1 g/L, CHTN-A was obtained from nano CHT (2 g/L) by dilution method



Conc of chitosan derivative in pad liquor 1 g/L, CHTN (A) was obtained from nano CHT (2 g/L) by dilution method

Figure 3.18 Effect of particle size of nano chitosan on absorbency of treated cotton fabric

3.3.10 Dyeing behaviour of nano chitosan treated cotton fabric

Chitosan pretreatment has shown improved dye uptake on cotton fibre both in presence and absence of electrolyte as discussed in chapter 2. However the dye was mostly confined to surface of fabric due to lack of penetration of parent chitosan. Fastness properties were also found to be deprecated. Thus, in this work, the effect of pretreatment of nano chitosan on direct dyeing of cotton was studied. In another approach, the dye bath was made slightly acidic with acetic acid (0.5 g/L) and treated for 15 minutes after the conventional dyeing was over (i.e. after the 60 minutes). The effects of chitosan and nano chitosan pretreatment on dye uptake are illustrated in Table 3.12 and graphically in Figures 3.19 and 3.20.

Table 3.12 Effect of particle size of nano-chitosan on dye uptake of treated cotton fabric

Parent chitosan			**Nano chitosan**				
Sample Code	**K/S Conventional dye bath**		**Sample Code**	**K/S**			
	C. I. Direct Red 81	**C. I. Direct Blue 71**		**C. I. Direct Red 81**		**C. I. Direct Blue 71**	
				Conventional dye bath	**Acidic dye bath**	**Conventional dye bath**	**Acidic dye bath**
Control	7.71	6.08	Control	7.71	6.33	6.08	4.94
CHT	9.07 *(17.6)*	6.99 *(14.8)*	CHTN-A	9.62 *(24.7)*	10.24 *(61.8)*	7.26 *(19.4)*	8.05 *(63.1)*
			CHTN	9.6484 *(25.1)*	10.39 *(64.2)*	7.43 *(22.1)*	8.12 *(63.4)*
CHT-D2	9.02 *(17.0)*	7.02 *(15.4)*	CHT-D2N	9.81 *(27.1)*	10.49 *(65.8)*	7.47 *(22.8)*	8.24 *(66.9)*
CHT-D3	9.05 *(17.3)*	6.81 *(12.0)*	CHT-D3N	9.83 *(27.4)*	10.51 *(66.2)*	7.72 *(26.9)*	8.25 *(67.1)*
CHT-D4	9.07 *(17.6)*	6.68 *(9.8)*	CHT-D4N	9.82 *(27.3)*	10.50 *(66.0)*	7.79 *(28.2)*	8.28 *(67.7)*
CHT-D5	9.10 *(18.0)*	7.09 *(16.5)*	CHT-D5N	9.96 *(29.1)*	10.60 *(67.5)*	7.81 *(28.3)*	8.38 *(69.7)*

Conc of chitosan derivatives in pad bath 1 g/L, Values in parenthesis indicate percent improvement in K/S compared with the corresponding control fabric sample

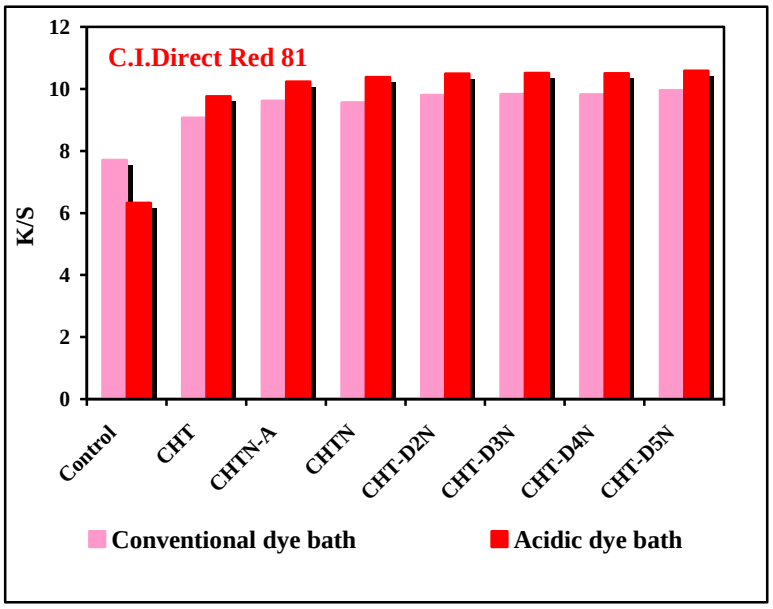


Figure 3.19 Effect of particle size of nano-chitosan on dye uptake of treated cotton fabric

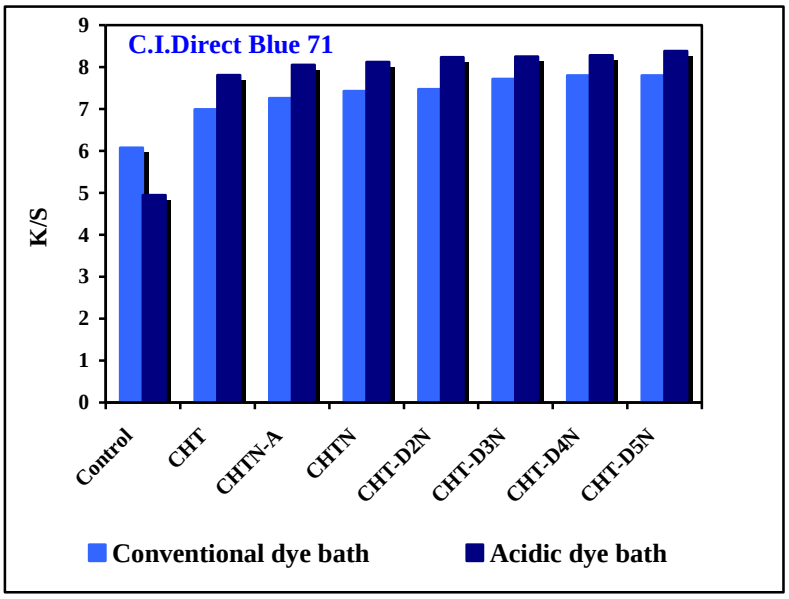


Figure 3.20 Effect of particle size of nano-chitosan on dye uptake of treated cotton fabric

Results revealed that the dye uptake by cotton fabric, in conventional process, increased marginally with normal chitosan treatment and further improved with the reduction in particle size of nano chitosan. On acidification, the dye up take was still increased compared to conventionally dyed samples. The increased dye uptake due to

chitosan treatment may be attributed to the presence of primary amino groups on chitosan. These cat ions dissipate the negative surface charge on cotton and drives dye molecules to the fibre. Further, the dye up take may also been enhanced due to the dyeability of chitosan itself with direct dyes. The nano chitosan due to increased surface area and hence higher accessibility for dye sites put much added value. The primary amino groups on chitosan get protonated in acidic medium having enhanced positive charge can now form salt linkages with anionic (sulphonate) groups of residual dye present in the dye bath. This leads to almost complete exhaustion of dye bath.

The washing fastness and rubbing fastness properties of direct dyed fabrics were also analyzed, which are presented in Table 3.13. The fastness to washing was found to be improved with reduction in particle size. This may be regarded to the formation of CHTN-Dye complex in situ. The fastness to rubbing was also slightly improved with decrease in particle size. This property is mainly associated with the rubbing fastness of dyes chitosan molecules on cotton fibre.

Table 3.13 Effect of particle size on fastness properties of direct dyes

Sample code	Particle size nm	C.I. Direct Red 81		C. I. Direct Blue 71	
		Wash fastness	Rub fastness	Wash fastness	Rub fastness
Control	-	3	2-3	4	2-3
CHT	4014	3	2	4	2
CHTN(A)	468.1	3-4	2-3	4-5	2
CHTN	319.4	3-4	2-3	4-5	2-3
CHT-D2N	271.6	3-4	2-3	4-5	2-3
CHT-D3N	231.0	4	2-3	4-5	2-3
CHT-D4N	195.2	4	2-3	5	3
CHT-D5N	110.7	4-5	3	5	3

Dyeing process: Conventional

3.3.11 Effect of nano chitosan on crease recovery property of cotton fabric

It is shown in previous chapter that the chitosan treatment adversely affected the wrinkle recovery property of cotton fabric. The molecular size of polymer was the major reason for this drawback. Reduction of the particle size of chitosan has found to enhance various properties at minimal concentration and is expected the possibility to restore the

aesthetics. The crease recovery property as a function of chitosan and nano chitosan treatments compared against commercial DMDHEU application and is presented in Table 3.14. The crease recovery angle of cotton fabric was greatly reduced by the treatment of normal chitosan (CHT). Treatment of cotton fabric with chitosan of lower particle size was found to improve the crease recovery property of cotton fabric. However yet it could not gain the rating of commercially used cross linking agent DMDHEU. Conventional chitosan is believed to form a surface coating which lowers the possibility of cross linking and therefore cannot contribute to the load sharing phenomenon. The improved wrinkle recovery property in case of nano chitosan treatment may be attributed to the greater penetration into fabric structure. These polycationic nano particles, due to better penetration, may bound the fibre molecules and resist creasing to some extent. However, a final touch up with conventional easy care finish is desired.

Table 3.14 Effect of particle size of chitosan on wrinkle recovery property of cotton fabric

Sample code	Conc in pad bath, g/L	Particle size, nm	Crease recovery angle (CRA°)		
			Warp	Weft	Total
Control	-	-	80	81	161
DMDHEU (40%)	20	-	85	95	180
	40	-	106	101	207
	60	-	112	113	215
CHT	1	4014	72	72	144
CHTN-A	1	468.1	79	79	158
CHTN	1	319.4	82	82	162
CHT-D2N	1	271.6	82	80	162
CHT-D3N	1	231.0	82	81	163
CHT-D4N	1	195.2	85	80	165
CHT-D5N	1	110.7	86	84	170

3.3.12 Effect of nano chitosan treatment on cotton fabric on its resistance against microorganism

Attributing to the polycationic nature, chitosan has shown resistance to microbial attack in soil burial test as discussed in chapter 2. The effect, however, was moderate and in order to improve the property the effect of particle size of nano chitosan was

examined. The antibacterial property of nano chitosan can further be enhanced by loading it with other antibacterial agents such as silver nano particle. Silver nano particles are very effective antimicrobial and antifungal agents at lower concentrations and are much more effective than other metals such as mercury, copper, lead, chromium and tin. At lower concentration, silver nano particles directly damage the cell envelope by penetrating the cell and then silver binds to the DNA, this complex prevents the DNA replication by displacement of hydrogen bonds between adjacent nitrogen of purines and pyrimidines [46]. Nano silver dispersion is produced by reduction of silver sulphate with sodium borohydride in presence of trisodium citrate under inert atmosphere, scheme 3.1. Nano silver colloid of concentration $1X10^{-3}$ M / 100 ml and average particle size 110 nm was prepared as published elsewhere [24].

$$4Ag^{+2} + NaBH_4 + 2H_2O \rightarrow 4Ag + BH_4 + Na^+ + 4H^+ + O_2$$

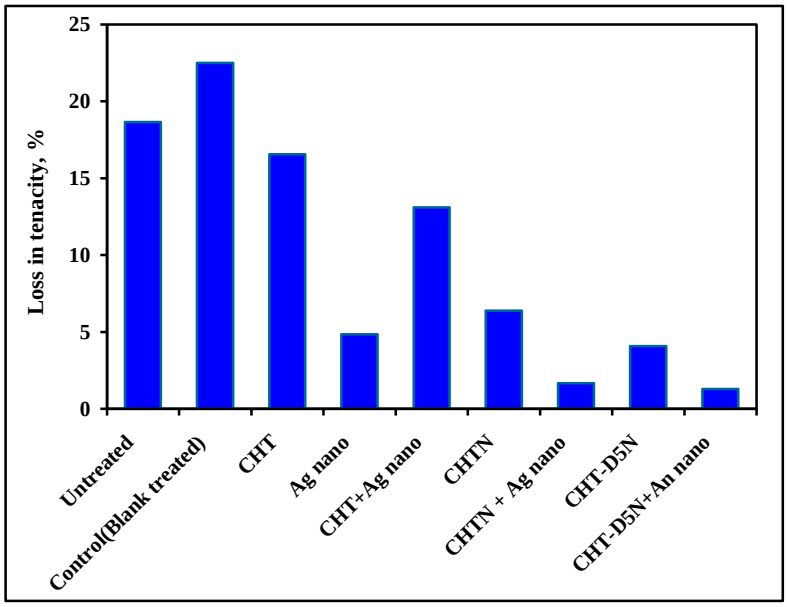
Scheme 3.1 Reduction of silver ions

Nevertheless it is extremely efficient antibacterial agent; its retention by the fibre for multiple washings is questioned. Attributing to the antibacterial and high metal particles retention properties of chitosan [47], the fabric was treated with chitosan (or nano chitosan) and then with nano silver colloid (two bath process). The resistance against bacterial attack of untreated and treated samples of cotton was determined by determining their loss in strength due to soil burial test. The results are presented in Table 3.15. It can be observed from these results that the chitosan can be employed as an efficient antibacterial agent. The effect is enhanced with the reduction in particle size of nano chitosan and coupling with nano silver.

Table 3.15 Effect of nano chitosan treatment on resistance towards microbial attack

Sample code	Particle size, nm	Tenacity, g/tex		*Drop in strength, %
		Before soil burial	After soil burial	
Untreated cotton fabric		23.33	18.98	18.65
Control		20.87	18.08	22.5
CHT	4014	20.48	19.47	16.55
Ag nano	110	22.68	22.20	4.84
CHT+ --------- Ag nano		24.51	20.27	13.10
CHTN	319.4	25.17	21.84	6.39
CHTN + ---------- Ag nano		24.21	22.94	1.67
CHT-D5N	110.7	25.72	22.38	4.07
CHT5N + --------- Ag nano		25.67	23.03	1.29

Control: Blank treatment was given with acetic acid (10 g/L) by pad-dry cure method,
**Drop in strength was measured from untreated cotton fibre*



Conc of chitosan derivative 1 g/L

Figure 3.21 Effect of nano chitosan on resistance towards microbial attack

REFERENCES

1. Charles P. Poole (Jr) and Frank J. Owens, *Introduction To Nanotechnology*, John Wiley & Sons, Inc., New Jersey (2003)
2. A.P.S. Sawhney, B. Condon, K.V. Singh, S.S. Pang, G. Li and David Hui, "Modern Applications of Nanotechnology in Textiles", *Textile Research Journal*, **78**(8) (2008), 731-739
3. R.Feyman, "Engineering and Science", **23**(5), February (1960) 22-36
4. http://www.nano.gov/
5. Abhilash Sugunan and Joydeep Dutta, "Nanoparticles for Nanotechnology", *Journal of Physics Science and Idea*, **4**(1&2) (2004) 50- 57
6. Bhupendra Singh Butola and Swana Mishra, "Nanotechnology in Textiles", *Asian Dyer*, **4** (01) Feb (2007) 70-76
7. Sorna Gowri, Luís Almeida, Teresa Amorim, Noémia Carneiro, António Pedro Souto and Maria Fátima Esteves, "Polymer Nanocomposites for Multifunctional Finishing of Textiles – a Review", *Textile Research Journal*, **80**(13), (2010) 1290–1306
8. H. C.Von Baeyer, "The Lotus Effect", *Sciences*, **40** (2000)12–15
9. Sabine Amberg-Schwab, "Functional coating using nanotechnology", *International Textile Bulletin*, No 1 (2004) 14-18
10. M. S. Inamdar, J. S Khan, A. V. Halbe and A. K. Khoja, "Prospects for Innovative Technologies in Textile Processing Industry", *Journal of Textile Association*, **66**(2), July-Aug (2005) 73-75
11. D. S. Schondelmair, R. Cramm, R. Klingeler, J. Morenz, C. Zilken and W. Eberhardt, "Orientation and Self Assembly of Hydrophobic Fluoroalkyl Silanes, *Langmuir* **18**, (2002) 6242–6245
12. Lei Qian and Juan P. Hinestroza, "Application of nanotechnology for high performance textiles", *Journal of Textile and Apparel, Technology and Management*, **4** (1) (2004) 1-7
13. Yang, H. Y., Zhu, S. K., and Pan, N., Studying the Mechanism of TiO2 as UV Blocking Additive for Fibers and Fabrics by an

Improved Scheme, *Journal of Applied Polymer Science,* **92**, (2003) 3201–3210

14. R.Q. Chen, "Nanometric Materials and Health Care Textiles", *Dyestuff Industries,* **39 (**2) (2002)4–28
15. R. H.Wang, J. H. Xin, Y. Yang, H. F. Liu, L. M. Xu, and J. H. Hu, "The Characteristic and Photo Catalytic Activities of Silver Doped ZnO", *Nano Cryst.,* **227** (2004)312–317
16. A. Bozzi, T. Yuranova and J. Kimi, "Self Cleaning of Wool-Polyamide and Polyester Textiles by TiO_2 Rutile Modifications Under Day Light Irradiation at Ambient Temperature", *Journal of Photochemistry and Photobiology A: Chemistry*, **172** (2005) 27–34
17. S. Y. Cui, Y. D. Zu, H. Q. Hui, and J. Y. Zhang, "Study on Antibacterial Properties of Nano Ceramics", *Journal Hebei University of Science Technology,* **24**, (2003)19–22
18. W. Athison, "Industrial Fabrics", *Prod. Rev.* **88**, (2003)12–17
19. T. Lopez-Leon, E.L.S. Carvalho, B. Seijo, J.L. Ortega-Vinuesa, D. Bastos-Gonzalez, "Physicochemical characterization of chitosan nanoparticles: electrokinetic and stability behavior", *Journal of Colloid and Interface Science*, **283** (2005) 344–351
20. Hong-liang Zhang, Si-hui Wu, Yi Tao, Lin-quan Zang, and Zheng-quan Su, "Preparation and Characterization of Water-Soluble Chitosan Nanoparticles as Protein Delivery System", *Journal of Nanomaterials*, **2010** (2010), 1-5
21. R. Bodmeier, H. Chen and O. Paeratakul, , "A Novel Approach to the Oral Delivery of Micro- or Nanoparticles", *Pharmaceutical Research*, **6** (1989) 413-417
22. K. L. Douglas and M. J. Tabrizian, "Effect of experimental parameters on the formation of alginate chitosan nanoparticles and evaluation of their potential application as DNA carrier" *Journal of Biomaterials Science, Polymer Edition*, **16** (2005) 43-56
23. Ştefania Racoviţă, Silvia Vasiliu, Marcel Popa and Cornelia Luca, "Polysaccharides Based On Micro- And Nanoparticles Obtained by Ionic Gelation and Their Applications As Drug Delivery Systems", *Revue Roumaine de Chimie*,

54(9) (2009) 709–718

24. D.P. Chattopadhyay and B.H. Patel, "Improvement in the physical and dyeing properties of natural fibres through pre-treatment with silver nanoparticles", *Indian Journal of Fibre & Textile Research*, **34**, December (2009) 368-373
25. V. R. Gowariker, N. V. Viswanathan, Y. Sreedhar, "Polymer Solutions", *Polymer Science,* First edition, New Age International Publisher, N. Dehli, India (1986) 332-362
26. Dunkan J. Shaw, "Rheology", *Introduction to Colloid and Surface Chemistry,* Fourth edition, Butterworth-Heinemann, Oxford (UK) (1992) 244-260
27. A.Tager, "Rheological properties of polymers in viscofluid state", *Physical Chemistry of Polymers,* MIR Publishers, Moscow (1972) 241-272
28. Kuo-Shien Huang, Yea-Ru Sheu, and In-Chun Chao, "Preparation and properties of nanochitosan", *Polymer -Plastics Technology and Engineering*, **48**, (2009) 1239- 1243
29. J. K. Patel and N. P. Jivani , "Chitosan Based Nanoparticles in Drug Delivery", *International Journal of Pharmaceutical Science and Nanotechnology*, **2**(2) July - September (2009)517-522
30. A. Berthold, K. Cremer, J. Kreuter, "Preparation and characterization of chitosan microspheres as drug carrier for prednisolone sodium phosphate as model for anti-inflammatory drugs", *Journal of Control Release*, **39** (1996)17-25
31. Mayyas M.A. Al-Remawi, "Properties of Chitosan Nanoparticles Formed Using Sulfate Anions as Crosslinking Bridges", *American Journal of Applied Sciences*, **9** (7) (2012) 1091-1100
32. L. Dambies, T. Vincent, A. Domard and E. Guibal, "Preparation of Chitosan Gel Beads by Ionotropic Molybdate Gelation", *Biomacromolecules*, **2** (2001) 1198-1205
33. H. Tokumitsu, H. Ichikawa, Y. Fukumori, Chitosan–gadopentetic acid complex nanoparticles for gadolinium neutron capture therapy of cancer: preparation by novel emulsion-droplet coalescence technique and characterization. *Pharmaceutical Research,* **16** (1999)1830-1835
34. Y.S. Leong, F. Candau, "Inverse microemulsion polymerization", *Journal of*

Physical Chemistry, **86** (1982) 2269-2271

35. S. Yu, J. Hu, X. Pan, P. Yao, M. Jiang, "Stable and pH-sensitive nanogels prepared by self-assembly of chitosan and ovalbumin", *Langmuir*, **22** (2006) 2754-2759
36. Y. Ohya, R. Cai, H. Nishizawa, K. Hara, T. Ouchi, "Preparation of PEG-grafted chitosan nano-particle for peptide drug carrier", *International Symposium on Control. Release Bioact. Mater*. **26** (1999) 655-656
37. I.F. Uchegbu, A.G. Schätzlein, L. Tetley, A.I. Gray, J. Sludden, S. Siddique, E. Mosha, "Polymeric chitosan-based vesicles for drug delivery", *Journal of Pharmacy and Pharmacology*, **50** (1998) 453-458
38. J. Gong, X. Hu, K. Wong, Z. Zheng, L.Yang, W. Lau,and R. Du, "Chitosan Nanostructures with Controllable Morphology Produced by a Nonaqueous Electrochemical Approach", *Advanced Materials*, **20** (2008) 2111–2115
39. R.A.A. Muzzarelli, 'Chitin Chemistry',*The polymeric materials Encyclopedia*, J.C. Salamone (ed), CRC press Inc, Boca Raton Fl, USA (1996) 312-314
40. Rong-Min Wang, Nai-Pu He, Peng-Fei Song, Yu-Feng He, Lan Ding and Zi-Qiang Lei, "Preparation of nano-chitosan Schiff-base copper complexes and their anticancer activity", *Polymers Advanced Technologies*, **20** (2009) 959–964
41. Worawan Boonyo, Hans E. Junginger, Neti Waranuch, Assadang Polnok and Tasana Pitaksuteepong, "Preparation and Characterization of Particles from Chitosan with Different Molecular Weights and Their Trimethyl Chitosan Derivatives for Nasal Immunization", *Journal of Metals, Materials and Minerals*, **18** (2) (2008) 59-65
42. Huacai Ge and Shiying Huang, "Microwave Preparation and Adsorption Properties of EDTA-Modified Cross-Linked Chitosan", *Journal of Applied Polymer Science*, **115** (2010) 514–519
43. B. Loretz and A . Bernkop–Schnürch, "In vitro evaluation of chitosan–EDTA conjugate polyplexes as a nanoparticulate gene delivery system", *AAPS J*, **8**(4), (2006) art. no. 85
44. J. Dutta and H. Hofmann, "Self-Organization of Colloidal Nanoparticles", *Encyclopedia of Nanoscience and Nanotechnology*, **9** (2004) 617-640

45. Boonyo Worawan, Junginger Hans E., Waranuch Neti, Polnok Assadang and Pitaksuteepong Tasana, "Preparation and Characterization of Particles from Chitosan with Different Molecular Weights and Their Trimethyl Chitosan Derivatives for Nasal Immunization", *Journal of Metals, Materials and Minerals,* **18**(2) (2008) 59-65
46. Natarajan Velmurugan, G. Gnana Kumar, Sang Sub Han, Kee Suk Nahm, and Yang Soo Lee, "Synthesis and characterization of potential fungicidal silver nano-sized particles and chitosan membrane containing silver particles", *Iranian Polymer Journal*, **18** (5) (2009) 383-392
47. Wen-Li Du , Shan-Shan Niu , Ying-Lei Xu , Zi-Rong Xu , Cheng-Li Fan, "Antibacterial activity of chitosan tripolyphosphate nanoparticles loaded with various metal ions", *Carbohydrate Polymers*, **75** (2009) 385–389

CHAPTER 4

SYNTHESIS AND CHARACTERIZATION OF *N*-SUBSTITUTED CHITOSAN DERIVATIVES AND THEIR APPLICATION ON COTTON FABRIC

4.1 INTRODUCTION

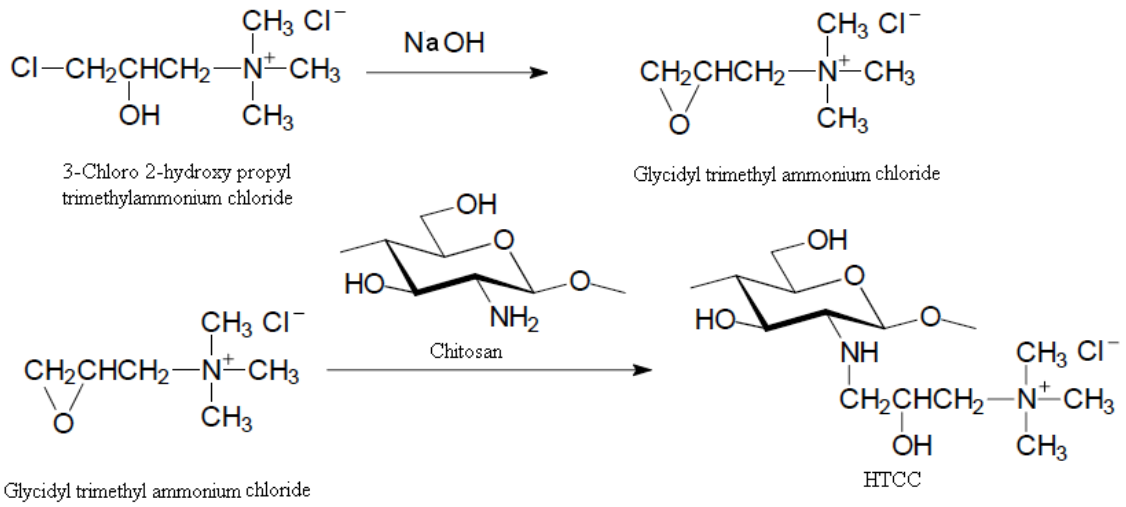
The application potential of chitosan biopolymer on cotton textiles is revealed in previous chapters. By virtue of polycationic nature and film forming properties, chitosan has proved a useful auxiliary in dyeing and finishing of cotton fabric. A substantial improvement in dyeability of chitosan treated fabric towards direct dyes from salt free dye bath was noticed. Post dyeing treatment of chitosan showed intensified colour value and improved fastness to washing. Resistance to microbial attack was also found to be improved. Besides improvements in these properties, the chitosan treated fabric, however, encountered several challenges. One of the major drawbacks of chitosan was its limited solubility in neutral or alkaline aqueous medium. Highly acidic pH required for solubility of chitosan resulted into hydrolytic degradation of fibre due to curing at elevated temperature.

The chitosan, due to higher viscosity and hence the rigid film deposited on surface of fibre, imparted undesired stiffness and harshness with result of loss in inherent appeal of cotton fibre. Further the appearance and wrinkle recovery property were found to be deteriorated. Lowering of viscosity by depolymerization of high molecular weight chitosan could not meet the requirements; on the other hand an excessive yellowness was imparted.

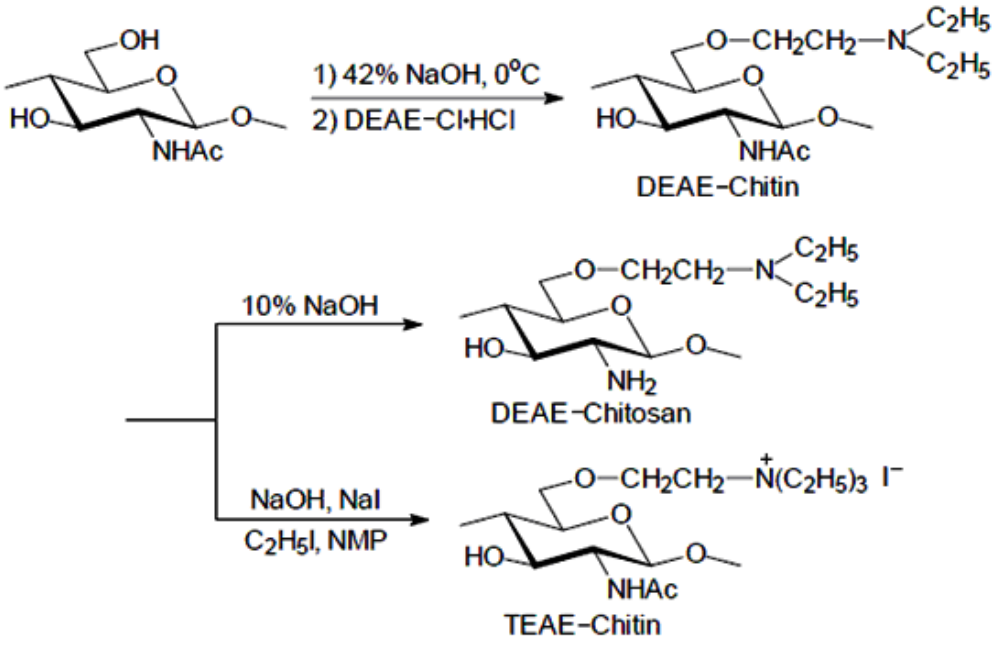
An emerging technology i.e. nano technology was adopted wherein the particle size of chitosan was scaled down to near nano level by ionic gelation with pentasodium tripolyphosphate (TPP). This enabled a greater penetration of polymer into the fibre structure and increased its effectiveness even at very low concentrations. Various properties, mentioned above, were found to be significantly improved. Nevertheless, stability of nano CHT dispersions was extremely limited and therefore standing bath stability was restricted to 24h.

In all cases, one of the severe problems encountered was loss in strength and whiteness due to chlorine retention (discussed in detail in section 4.3.2.3). Chlorine retention mainly arises due to the presence of free -NH- groups [1] which form chloramines with chlorine in presence moisture particularly in absence of alkali causing the yellowness. Chloronitrogen compounds thus formed liberate hydrochloric acid during heat treatments like pressing under moist condition, which damage the cloth. A very similar kind of problems often found in finishing treatments with aminoplasts and cationic softeners containing free -NH- groups [2, 3] as illustrated in scheme 4.13. In order to avoid or minimize such damages due to either acid hydrolysis during curing process or due to chlorine retention, structural modifications in chitosan are essential such that aqueous solubility at almost neutral pH is obtained and /or modifying the amino functional groups by replacing their free protons by other stable groups so that no sites available for chlorine retention. The limited solubility of chitosan in aqueous media can be overcome by introducing new functionalities through its derivatization such as, for instance, sulphonation [4], sulphation [5], carboxymethylation [6], grafting [7, 8] etc reactions. Grafts of chitosan and polyacrylic acid have shown very high water-sorbing ability (~ 600% w/w) [9]. Such reactions, however, also add an anionic nature to the cationic polyelectrolyte character of the parent chitosan [10]. These reactions, often, occur at hydroxyl reactive sites [11]. *N*-substituents containing water dissolving moieties can be obtained by selectively halogen displacement reaction [12] or by reductive amination [13] to produce products like *N*-caboxymethyl chitosan, *N*-carboxypropyl chitosan etc derivatives.

An alternative route to improve the water solubility of chitosan without changing its cationic character is the introduction of an enough number of permanent positive charges in its chains. One such method is the attachment of substituent bearing quaternary ammonium terminal group. A product containing *N*- substituted quaternary ammonium salt namely *N*-(2-hydroxy) propyl -3-trimethyl ammonium chitosan chloride (HTCC) was synthesized by Daly and Guerrini [14] by using a compound that produces the glycidyl reagent *in situ* such as 3-chloro-2-hydroxy propyl trimethylammonium chloride, a commercially available stable compound Quat 188, developed (Scheme 4.1) This Chitosan derivative (HTCC) shows excellent solubility in neutral water.



Scheme 4.1 Synthesis of *N*-(2-hydroxy) propyl -3-trimethyl ammonium chitosan chloride (HTCC)



Scheme 4.2 Synthesis of *O*-substituted quaternary ammonium chitin and chitosan

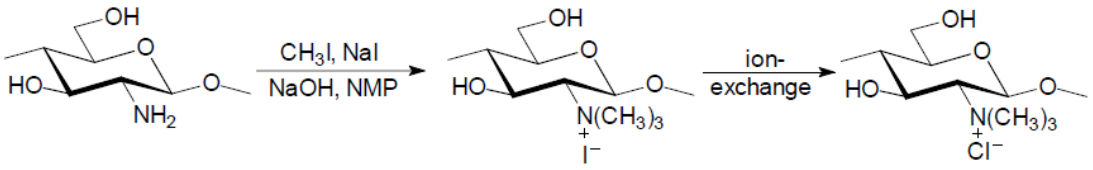
Quaternary ammonium group containing substituents can also be attached through *O*-substitution reaction. Kim et al [15] obtained triethylaminoethyl derivative of chitin

(TEAE-Chitin). It was synthesized by first activating the C-6 primary hydroxy group in chitin at low temperature. The activated chitin was then allowed to react with diethylaminoethyl chloride (DEAE) to produce DEAE-Chitin derivative, followed by quaternization using ethyl iodide. Interestingly, the intermediate DEAE-Chitin derivative was also found soluble at neutral pH. These products on deacetylation gave chitosan derivatives as illustrated in scheme 4.2

All these reactions, however, could not obviate the free -NH- groups completely and the problems associated with chlorine retention still persisted. Modifications of amino groups of chitosan or above derivatives though substitution reactions such as complete alkylation or in other words direct quaternization of amino groups can produce chitosan tri alkyl ammonium halide salts or quaternary ammonium salts which are totally -NH- free. A simplest derivative in this class is the trimethylammonium salt of chitosan. It is obtained by repeated treatment of chitosan in *N*-methyl-2-pyrrolidone (NMP) containing sodium iodide and methyl iodide in presence of sodium hydroxide. An anionic exchange of iodide with chloride ion may be necessary due to stability issues. The quaternization reaction is shown in scheme 4.3. Bayat et al [16] studied the effect of sodium hydroxide and methyl iodide concentration on degree of quaternization and found these to be the most effective reaction variables. Most of previous researchers have followed the same protocol for the synthesis of chitosan alkyl ammonium halide salts [17-20]. Attempts have also made in synthesizing *N*-methyl chitosan derivatives in acidic medium, as reviewed by Achwal [21] from German literature. In this method, chitosan was dissolved in 1% acetone and pH was adjusted to 6.3 and then refluxed at boil with excess methyl iodide for 10h.

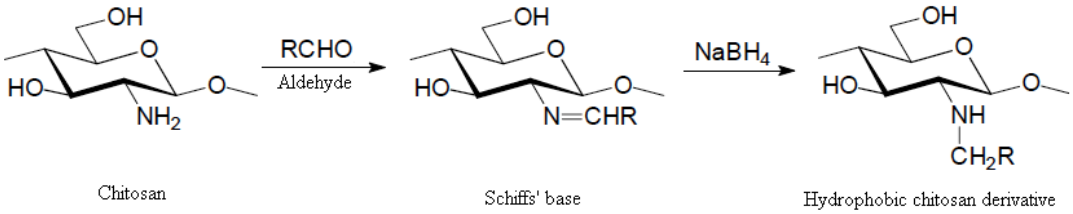
Reductive amination i.e. Bosch reduction of Schiff's base provides an attractive route for the synthesis of *N*-substituted chitosan compounds containing alkyl or aryl groups of varying chain lengths or molecular sizes. Primary amines when treated with alkyl or aryl aldehydes produce Schiff's base which on reduction with $NaBH_4$ or $NaBH_3CN$ results into *N*-alkyl or aryl substituent becoming secondary amine [22] as shown in scheme 4.4. Since the reaction is carried out in acidic medium, a great degree of homogeneity is favored. These secondary amines then can further be quaternized with alkyl iodide similar to scheme 4.3. A series of chitosan quaternary ammonium salts

containing *N*-alkyl and/or *N*-aryl substituents were prepared by different workers for various purposes are reported [16, 18, 23-28].



Chitosan | Trimethylammonium iodide salt | Trimethylammonium chloride salt

Scheme 4.3 Synthesis of trimethylammonium salt of chitosan



Chitosan | Schiffs' base | Hydrophobic chitosan derivative

Scheme 4.4 Synthesis of hydrophobic chitosan derivatives: Bosch reduction

Studies related to synthesis, properties and applications of chitosan derivatives such as quaternary ammonium salts, *N*-alkylated, *N*-arylated and combination of these are reported in literature. Muzzarelli and Tanfani [29] followed the reductive amination Schiff's base and then methylation of N-alkyl chitosan to generate prepared *N*-trimethyl chitosan iodide salt. This three step method was found to reduce DP of main chain and resulted side reactions such as *O*-substitution. This effort was made, aiming its application as antibiotic and ion exchange material. Britto and Assis used dimethylsulfate for obtaining quaternary ammonium salt [30].

With respect to its physical and chemical properties several works have been published. Curti and Filho [31] studied the viscosity behaviour of trimethyl chitosan chloride salt. Their study showed that the chitosan and trimethyl chitosan chloride exhibit a linear decrease in intrinsic viscosity as a function of reciprocal square root of the ionic

strength. The molecular weight was found to be affected due to quaternization maintaining the chain stiffness intact. Snyman et al [19] prepared varying degree of trimethyl chitosan chloride by repeated quaternization treatments. The weight average molecular weight and intrinsic viscosities were found to be decreased with increase in degree of quaternization due to repeated processes. Britto et al. [32] observed the changes in mechanical properties due to *N*-methylation of chitosan. Films of chitosan and trimethyl chitosan presented viscoelastic behaviour, where in the former exhibited elastic behaviour with greater elongation while the latter had small modulus of elasticity and typical viscous behaviour. These authors [33] also reported a kinetic study on thermal degradation of trimethyl chitosan.

Murata et al. [34, 35] reported the cytotoxic activity and the formation of polyelectrolyte complex trimethyl chitosan with DNA. Kean et al. [36] and Thanou et al. [37] published results of a study about the toxicity and transfection efficiency of trimethyl chitosan derivatives with respect to the degree of quaternization. As trimethyl chitosan gained attention for use in oral drug delivery, some reviews on the subject have appeared [38 - 40]. The quaternary ammonium salt using glycidyl trimethylammonium chloride as the quaternizing agent was found to be useful in cosmetic applications [14]. Kotze et al. [41] found a superior efficiency as absorption enhancer for hydrophilic drugs across intestinal epithelia than the chitosan itself.

Various long chain alkyl substituents have resulted in chitosan derivatives with varying degree of hydrophobicity. Such materials are industrially important as they show unusual and interesting rheological properties thought to arise from the intermolecular association of neighboring hydrophobic substituents [42]. More recently, an important branch of application for chitosan quaternary salt related to antimicrobial action has gained attention. It started by Kim et al. [23, 43] testing several chitosan quaternary salt against *Staphylococcus aureus*. In this way, the authors described the reaction of chitosan with formaldehyde, butyraldehyde, n- octyl aldehyde, and n-dodecyl aldehyde, treated the resulting Schiff's bases with sodium borohydride, obtaining the quaternary salts via methyl iodide synthetic route. In fact, the antibacterial activity of the prepared salts was higher than that found for chitosan itself and increased with increasing chain length of the alkyl substituent. Jia et al. [44], also prepared several quaternary chitosan salts and tested

against gram-negative bacteria *Escherichia coli*. It was seen that these salts exhibited higher *in vitro* activity against *E. coli* than chitosan, mainly in acid medium. Particularly, other combinations including alkyl, aryl moieties and carboxymethylation in chitosan quaternary salt also showed to be efficient against gram-negative and gram-positive bacteria [27, 45-47]. Effect of different *N*-substituents on insecticidal and fungicidal activity of chitosan is presented by Rabea et al [24, 25]. They found all the *N*-alkylated and *N*-benzyl chitosan derivatives higher fungicidal activity than parent chitosan against *Botrytis cinerea* and *Pyricularia grisea*, and a derivative *N*-(2-chloro 6-fluorobenzyl) benzyl chitosan as a most effective insecticide.

The utmost research is the synthesis and application of chitosan quaternary salts as nanoparticles. The most popular method of preparation of nano dispersion of chitosan quaternary salts is based on ionic gelation process with TPP. Xu et al. [48] synthesized *N*-(2-hydroxyl) propyl -3-trimethyl ammonium chloride nanoparticles. They described nanoparticles in the size range of 110 to 180nm with enhanced protein carrier efficiency. Several other important applications have emerged for chitosan trimethyl ammonium salts nanoparticles, such as nasal [49, 50] and oral vaccine delivery system [51]; and insulin releaser [52].

Thus, broadly speaking, the applications of these chitosan derivatives are emphasized mostly in medical domain such as gene delivery tool, controlled drug release system, as absorption enhancer for hydrophilic drugs transport across epithelium, antibiotics and, in cosmetics. However, very few applications of chitosan quaternary ammonium salts on textiles are reported. Most of the applications studied were antimicrobial concern. Kim et al.[53] treated the cotton fabric with HTCC and studied the effect on antimicrobial property. At very low concentration, such as 0.025% o.w.b., HTCC showed very superior antibacterial property, indicated by almost 100% reduction in bacteria as against only 30% reduction in bacteria in case of 1% chitosan. Lim and Hudson [54] treated the cotton fabric with fibre reactive chitosan derivative containing quaternary ammonium groups, *O*-acrylamidomethyl- *N*-(2-hydroxy) propyl -3-trimethyl ammonium chitosan chloride (NMA-HTCC) and evaluated its effect on dyeing with direct and reactive dyes; and antibacterial properties. They reported enhanced dye uptake with zero salt concentration with improved fastness properties. The antibacterial effect of

cotton treated with 1% NMA-HTCC, however, was almost lost after dyeing. This was attributed to the blocking of cationic groups. The undyed cotton fabric treated with 1% NMA-HTCC, on the other hand, showed 100 % reduction in bacteria which was sustainable for 50 wash cycles as against only 30% bacterial reduction by parent chitosan. Gleanings from German literature by Achwal [55] reported the after treatment with *N*-methyl chitosan derivative showed good improvement in fastness of direct dyeings comparable with conventional synthetic products.

The present research work, therefore, has been aimed at preparing a series of chitosan derivatives belonging to *N*-substituted quaternary ammonium salts having enhanced hydrophilicity and reducing free of -NH- groups presence to capture chlorine in any post treatment. Trimethyl chitosan chloride (TMCHT) was synthesized by the reaction of chitosan (CHT) with methyl iodide in alkaline medium followed by ion exchange with sodium chloride. In another series of chitosan derivatives, *N*- alkyl and *N*-aryl substituted chitosan of varying molecular size of substituents through the reductive amination of Schiff's base obtained by the reaction of chitosan with respective aldehydes were synthesized. The quaternization of *N*-substituted derivatives were then performed by the reaction of these compounds with methyl iodide as was carried out for TMCHT. The selected *N*-alkyl chitosan derivates were *N*-ethyl chitosan (N-Et CHT), *N*-butyl chitosan (N-Bu CHT) and *N*-dodecyl chitosan (N-Dod CHT) and that of *N*-aryl substituents were *N*-benzyl chitosan (N-Bz CHT) and *N*-(1-Naphthyl) methylene chitosan (N-Np CHT) derivatives. These *N*-synthesized chitosan derivatives were further quaternized with methyl iodide in alkaline medium. Various techniques employed for characterization of these derivatives were FTIR spectroscopy, ^{1}HNR spectroscopy, Elemental (CHN) analysis and conductometry. Various reaction parameters such as methyl iodide concentrations, alkali concentration and the role of co-solvent (NMP) on degree of quaternization of chitosan were studied. The further study performed also include effect of chain length of alkyl substituent and molecular size of *N*-aryl substituent on degree of substitution on CHT and also on then quaternization (DQ) of *N*- substituted CHT derivatives.

Trimethyl chitosan chloride (TMCHT) of varying degree quaternization and *N*-substituted CHT of similar level of DS and the quaternized derivatives of maximum DQ

on these selected *N*- substituted CHT were applied to cotton fabrics by pad dry cure method. Effect of these *N*- substituted CHT derivatives at different concentrations on the appearance, feel, chlorine retention, absorbency, dyeing behaviour with direct dyes that including both pre and post dyeing treatment were studied. Absorbency was determined by drop penetration method and handle by measuring the bending length. The dyeing behaviour was also extended to evaluate the stoichiometry by dyeing with acid dye. Appearance and dyeing results were examined on computer colour matching systems in terms of whiteness, yellowness brightness indices and K/S values respectively. The effect of CHT derivatives on cotton fabric was also studied for various aesthetics and value additions such as wrinkle recovery, soil release and antimicrobial properties. The resiliency was determined by crease recovery angle and compared with commercial aminoplast resin. The soiling tendency towards oily soil was evaluated both gravimetrically and optically on CCMS. Resistance to microbial attack was studied by evaluating the strength loss due to rotting under composted soil bed i.e. soil burial test.

4.2 MATERIALS AND METHODS

4.2.1 Fabric

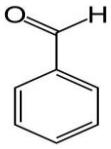
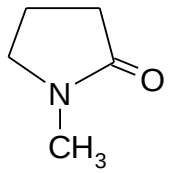
The same fabric as specified in chapter 2, section 2.2.1 was used.

4.2.2 Dyes and chemicals

The details of various chemicals employed in present research investigation are given in Table 4.1.

Dyes namely C.I.Direct Red 81, C.I.Direct Blue 71, C.I. Acid Blue 158 and chemicals namely Chitosan (CHT), DMDHEU etc used were the as specified in chapter 2, section 2.2.1. and other chemicals such as acetic acid (CH_3COOH), acetone (CH_3COCH_3), Glauber's salt (Na_2SO_4), methyl alcohol(CH3OH), magnesium chloride ($MgCl_2$), potassium iodide (KI), sodium iodide (NaI), sodium hydroxide (NaOH), sodium chloride (NaCl), soda ash(Na_2CO_3), silver nitrate ($AgNO_3$) etc used were of analytical grade obtained Qualikem Fine Chemicals Pvt Ltd, Vadodara. Double distilled was employed for all synthesis and analytical purposes.

Table 4.1 Specifications of various chemicals

Sr no	Name and Supplier	Specifications
1.	Methyl Iodide (MeI), Qualikems Fine Chem Pvt. Ltd	Grade: Analytical, Purity 99%, Mol.wt 142, Density 2.28g/cc Molecular Formula: CH_3I
2.	Acetaldehyde (35%), s.d.fine chemicals Ltd, Mumbai	Grade A.R, Purity 35%, Mol wt 44.05, Density 0.78 g/cc Chemical Formula: CH_3CHO
3.	n-Butyraldehyde Spectrochem Pvt Ltd, Mumbai	Grade: Analytical, Purity 99%, Mol wt 72.11, Density 0.8 g/cc Chemical Formula: $CH_3(CH_2)_2CHO$
4.	Dodecyl Aldehyde Acros Organics Fisher Scientific	Grade: Analytical, Purity 92%, Mol wt 184.32, Density 0.83 g/cc Chemical Formula: $CH_3(CH_2)_{10}CHO$
5.	Benzaldehyde Finar Chemicals Ltd., Ahmedabad	Grade: Analytical, Purity 99%, Mol wt 106.13, Density 1.044 g/cc Chemical Formula: C_6H_4CHO 
6.	1-Napthaldehyde Acros Organics Fisher Scientific	Grade: Analytical, Purity 95%, Mol wt 156.18, Density 1.15 g/cc Chemical Formula: $C_{10}H_7CHO$
7.	Sodium borohydride Qualikem Fine Chemicals Pvt Ltd, Vadodara	Grade: Analytical, Purity 97%, Mol wt 37.83, Chemical Formula: $NaBH_4$
8.	N-Methyl 2-pyrolidone (NMP), Qualikem Fine Chemicals Pvt Ltd, Vadodara	Grade A.R, Purity 93 %, Mol. Wt 99.13, Density 1.028g/cc Chemical Formula: C_5H_9NO 

4.2.3 Synthesis of *N, N, N*-Trimethyl chitosan chloride

The *N*-methylation reaction of chitosan aiming the preparation of *N, N, N*-trimethyl chitosan chloride was carried out with little modification as described elsewhere [31, 37, 50] as follows: purified chitosan (CHT) 1.0 g (corresponding to 90

m.mol of -NH_2) was suspended in NMP (40 ml) in a stainless steel reaction vessel and the suspension was kept at room temperature with constant stirring for 24 h. Then, sodium iodide 2.4 g, aqueous sodium hydroxide (20 %, 10 ml) i.e.2 fold excess of CHT and methyl iodide 5 g i.e. 5 fold excess of CHT (molar concentration, 1g CHT corresponds to 0.913 g. eq. rounded to 1.0 g. eq. of methyl iodide) were added. The vessel was sealed and run for 1h at room temperature on glycerin bath. The temperature was then raised to 50^0C and treated at this temperature for another 24 h. The clear dark brown liquid so obtained was poured in excess acetone to precipitate out the iodide of trimethyl chitosan. This precipitate was washed 3 to 4 times with acetone. This iodide salt was then subjected to ion exchange by treatment with 50 ml of sodium chloride 10% for 1h. Trimethyl chitosan chloride was then recovered from acetone as above and oven dried at 55^0C. Sample of different degree of quaternization were also prepared by varying the concentrations of methyl iodide as given Table 4.2. These samples were nomenclatured as TMCHT.

4.2.4 Synthesis of *N*-Alkyl and *N*-Aryl chitosan derivatives

The *N*-substitution of chitosan was carried out according to methods described in literature [23, 24, 27]. In general, purified CHT 1g (corresponding to 90 m.mol of -NH_2) was dissolved in acetic acid (1%) solution. Required concentration of aqueous aldehyde, listed in Table 4.11, was added gradually to CHT solution at room temperature and stirred for 2 h. The pH of the rection medium was adjusted to 4.5 using few drops of dilute sodium hydroxide solution and then sodium borohydride (10 % aqueous solution) 1.5 fold excess of aldehyde was added very gradually and the stirring was continued for 2h. The precipitate of the *N*-substituted CHT derivative was recovered from alkaline solution at pH 10 by adding sodium hydroxide solution (10%) and then washed thoroughly with distilled water to neutrality. The unreacted aldehyde and other impurities were removed by refluxing with methanol and diethyl ether and then oven dried at 55^0C. The *N*-substituted CHT derivative was then quaternized with methyl iodide as described in section 4.2.3.

4.2.5 Fabric treatment with chitosan and chitosan derivatives by pad-dry cure process

Same method was followed for the application of chitosan derivatives as described in chapter 2, section 2.2.5.

4.2.6 Dyeing with direct dyes

Dyeing with direct dyes and the evaluation of colour depth (K/S) and fastness properties were done as described in chapter 2, section 2.2.7.

4.2.7 Dyeing with acid dyes

Dyeing with acid dyes and the evaluation of colour depth (K/S) were carried out as described in chapter 2, section 2.2.8.

4.2.8 FTIR spectra analysis

FTIR of chitosan and chitosan derivatives were determined using the same method described in chapter 2, section 2.2.11.

4.2.9 ^{1}H-NMR spectra analysis

^{1}H-NMR spectra of chitosan and *N*-modified chitosan derivatives were determined using the same method described in chapter 2, section 2.2.12.

4.2.10 Elemental analysis

Elemental analysis of CHT and *N*- substituted CHT were carried using the method described in chapter 2, section 2.2.13.

4.2.11 Measurement of pH of liquor

The pH of solution was determined using pocket size pH meter (Hanna Instruments, Model HI96107)

4.2.12 Conductometric titrations

To determine the degree of quaternization, TMCHT (or quaternized sample) 0.5g was dissolved in water 100 ml containing acetic acid 1ml. The solution was titrated against 0.1M $AgNO_3$ solution conductometrically (Systronics make DDR conductivity meter, model no 304) using platinum electrode cell with cell constant 1.02. The conductance (mMhos) was plotted against burette reading (0.1M $AgNO_3$ solution, ml) to obtain the '*V*' value at lowest conductance. Average of three readings was considered for the calculation. The degree of quaternization (D.Q) can be calculated using following equation.

$$\text{DQ (\%)} = \frac{M_Q \times V \times [AgNO_3]}{m} X100 \qquad \textbf{(4.1)}$$

Where,

M_Q is the molecular weight (g/mol) of repeating unit of TMCHT containing quaternized site, V and [$AgNO_3$] are the equivalent volume and concentration of $AgNO_3$ aqueous solution (0.1M) respectively, and m (g) is the mass of TMCHT.

4.2.13 Determination of viscosity

The viscosity of chitosan and chitosan derivatives solutions was measured using the capillary method as described in chapter 2, section 2.2.10.

3.2.14 Determination of appearance and stiffness of fabric

Determination of appearance indices and stiffness of fabric samples were done as described in chapter 2, sections 2.2.15 and 2.2.16 respectively.

4.2.15 Evaluation of strength loss due to chlorine retention

The strength loss due to chlorine retention was determined according to AATCC Test Method 114-2005. A specified size sample (5 X 5 cm) was treated with sodium hypochlorite solution (1g/L) having 50:1 liquor-to-cloth ratio. The reaction was carried out at room temperature for 15 minutes followed by thorough rinsing and air drying. The

air dried sample was then subjected to steaming under pressure 30psi at 120 ^{0}C for 30 minutes. The strength in terms of tenacity (g/tex) of treated and untreated samples was stelometer (SITRA, Coimbator, India) and the strength loss was calculated below formula.

$$\text{Strength loss (\%)} = \frac{A - B}{A} \times 100 \qquad \textbf{(4.2)}$$

Where, A and B are the tenacity (g/tex) of untreated and treated samples respectively.

The loss in whiteness was determined by measuring the yellowness index (2 deg. / C/ ASTM D 1925) on computer colour matching system (Spectroscan 5100A, Premier Colorscan, Mumbai). In order to intensify the yellowness for faster evaluation, the samples were treated with solution containing potassium iodide (10g/L) and acetic acid (10 g/L) for 15 minutes and rinsed. The colour is intensified due to reaction of chloramines with potassium iodide to liberate iodine corresponding to the amount of chlorine retained on fabric [1].

4.2.16 Determination of tenacity

The tenacity and elongation of treated and untreated cotton fibres were measured on Stelometer as described in chapter 2, section 2.2.9. The tenacity was calculated using following formula.

$$\text{Tenacity (g/tex)} = \frac{\text{Breaking Load (kgs)} \times 1.5 \times 10}{\text{Sample Weight (mg)}} \qquad \textbf{(4.3)}$$

Sample Length = 1.5 cm

4.2.17 Determination of absorbency and crease recovery angle of fabric

Determination of absorbency and crease recovery angles of fabric samples were done as described in chapter 2, sections 2.2.17 and 2.2.18 respectively.

4.2.18 Evaluation of soiling behaviour

Soil release properties of CHT and its derivatives treated cotton fabric were evaluated according to AATCC Test Method 151-1990 with little modifications. In brief, a fabric swatch (10 X 10 cm) was treated with standard soil, prepared from vacuum cleaner dirt (100 g) and olive oil (3g), of 80% o.w.m. for 30 minutes in a stainless steel tumble in presence of glass balls (Nos 20, Dia 1.5 cm). The superficial dirt of soil treated sample was then removed by shaking in air and subjected for caging for 15 minutes (twice). The sample was then given soaping treatment at 60 ^{0}C for 30 minutes with gentle stirring with 10 g/L detergent (Ezee detergent, Godrej) with liquor to material weight ratio of 50:1 and then rinsed thoroughly and oven dried at 105 ^{0}C. The dried samples were preserved in desiccator for 24 hrs, weighed and the amount of soil retained was calculated using following formula.

$$\text{Soil retention}(\%) = \frac{\text{Final Weight (g) - Initial Weight (g)}}{\text{Initial Weight (g)}} \times 100 \qquad \textbf{(4.4)}$$

The unsoiled and soiled samples were also evaluated on Spectroscan 5100A (Premier Colorscan) for reflectance (% R), K/S values and yellowness index (2 deg / C/ ASTM D 1925) to determine degree of soiling [56, 57] using following expression.

$$\text{Degree of Soiling} = (K/S)_S - (K/S)_U \qquad \textbf{(4.5)}$$

Where, $(K/S)_U$ is the K/S value of unsoiled sample and $(K/S)_S$ that of soiled sample.

4.2.19 Soil burial test

The untreated and treated samples were subjected to soil burial test as per AATCC Test Method 30-2004 as described in chapter 2, section 2.2.19.

4.3 RESULTS AND DISCUSSION

4.3.1 Synthesis and characterization

An objective of the present investigation was in part synthesizing a series of *N*-substituted chitosan derivatives and imparted with quaternary ammonium functionality and then evaluation of their performance on cotton fabric. This was approached by

synthesizing *N*-chitosan derivatives of three categories, viz, trimethyl chitosan chloride, *N*-alkyl substituted quaternized chitosan and *N*-aryl substituted quaternized chitosan.

The main parameters that characterize these chitosan derivatives are degree of substitution (DS) and/or degree of quaternization (DQ). The DQ was determined by conductometric titrations with standard sliver nitrate solution. Instrumental methods like CHN analysis and ^{1}HNMR spectroscopy were employed for the quantitative estimation of both DS and DQ. The usefulness of FTIR spectroscopy on *N*-substituted chitosan characterization was mainly employed for qualitative analysis only. Structural modifications of chitosan due to the introduction of methyl and other substituents were characterized by the analysis of FTIR spectra. Viscometry was conducted for the comparative study of aqueous behaviour and molecular weight related properties of these derivatives.

4.3.1.1 Synthesis of N, N, N-trimethyl chitosan chloride

N, N, N-trimethyl chitosan chloride (TMCHT) was synthesized by the treatment of chitosan in *N*-methyl-2-pyrrolidone (NMP) containing sodium iodide and methyl iodide in presence of sodium hydroxide. An anionic exchange of iodide with chloride ion was then followed to get more stable chloride salt as shown in reaction scheme 4.3. The quantities of various ingredients taken for the reaction are enlisted in Table 4.2.

Table 4.2 Various ingredients used for the synthesis of TMCHT

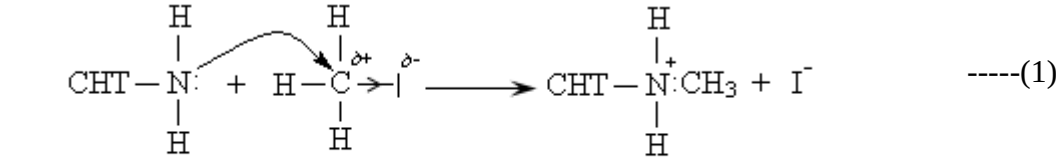
Sample	Methyl Iodide, g	NMP, ml	CHT:NaOH	CHT:NaI
TMCHT1	5	40	1:2	1:2.4
TMCHT2	10	40	1:2	1:2.4
TMCHT3	15	40	1:2	1:2.4

All these concentrations are calculated for 1g CHT

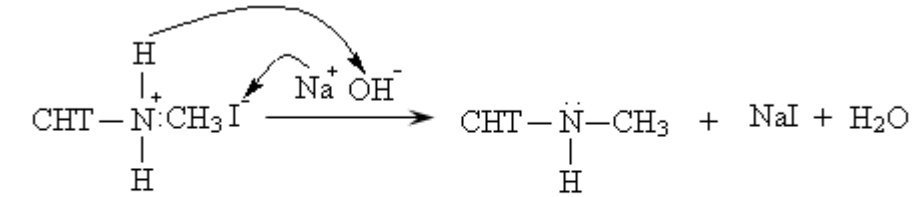
4.3.1.1.1 Reaction mechanism

The primary amino groups of chitosan, due to presence of unshared pair of electrons, act as strong nucleophiles (CHT-$N^{\delta-}H_2$). These nucleophiles bond to and yield

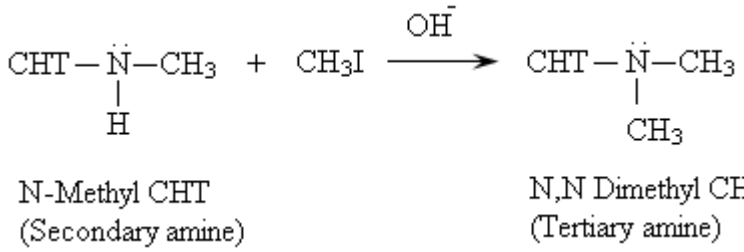
products with a variety of electrophiles, so the methylation reaction proceeds via electrophilic substitution.



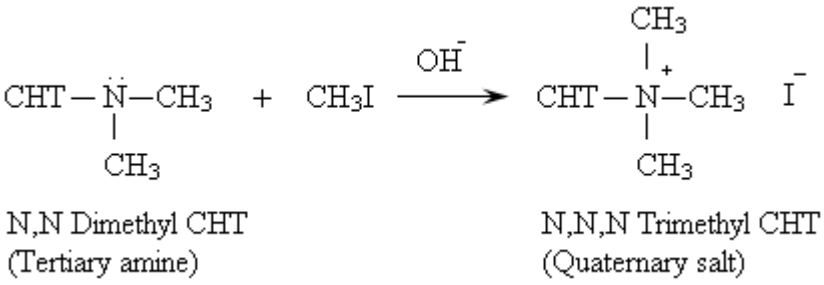
-----(1)



-----(2)



-----(3)



-----(4)

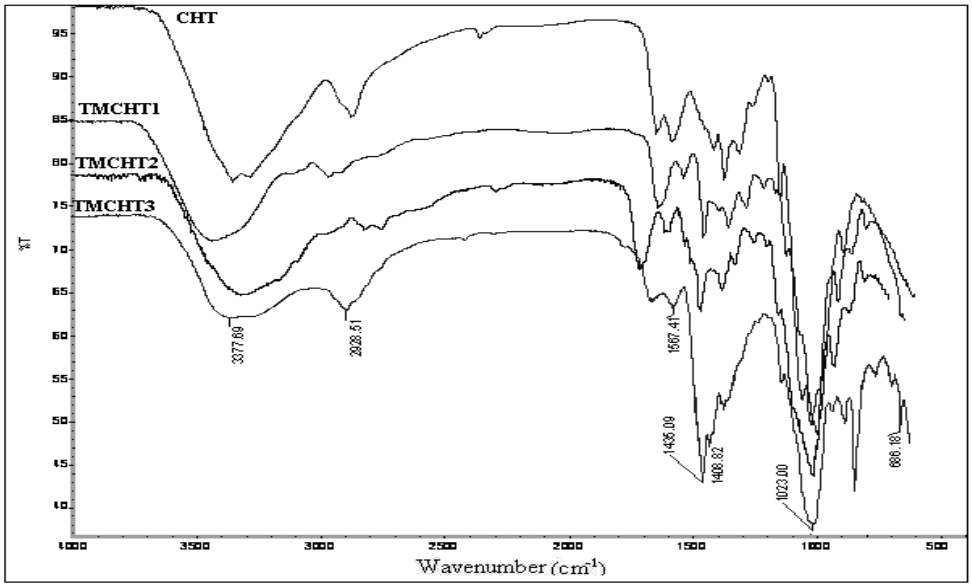
Scheme 4.5 Electrophilic substitution reaction: Methylation of CHT

In alkyl halides e.g. methyl iodide on the other hand, the electronegative iodine due to induction effect pulls electrons towards it and make the methyl carbon electron deficient

i.e. electrophilic ($H_3\mathbf{C}^{\delta+}$–$X^{\delta-}$). The reaction between nucleophilic amines and electrophilic methyl iodide proceeds presumably by a S_N2 mechanism and produce methyl chitosan ammonium salt (CHT-Methyl cation). The methyl chitosan ammonium salts in presence of alkali immediately gives secondary amines. The secondary amine undergoes similar reaction with second molecule of methyl iodide to form tertiary amine. The tertiary amine finally reacts with third molecule of methyl iodide to quaternary ammonium salt. Since this reaction system is heterogeneous, a progressive methylation of amines is most probable and possibly gives mixture of mono, di and trimethyl chitosan derivatives [22, 58]. The overall reaction mechanism is illustrated in scheme 4.5.

4.3.1.1.2 FTIR spectra analysis

The FTIR spectra of CHT and various grades of TMCHT are presented in Figure 4.1. The amino and hydroxyl functional groups in chitosan molecule are characterized by a broad band absorption peak in FTIR spectrum at wavenumber 3355 cm^{-1}, which are due to O-H and N-H stretching vibrations. The amino group is characterized by a weak absorption peak at 1585 cm^{-1} due to N-H bending vibrations [59]. Reduction in intensity of these absorption peaks in quaternized chitosan indicates the removal of H of $-NH_2$ groups of chitosan and the formation of new peak at 1470 cm^{-1} corresponds to asymmetrical C-H stretching of methyl ($-CH_3$) group which is introduced through quaternization reaction [18, 23, 59]. With increase in degree of quaternization the intensity of peaks at 3355 and 1585 cm^{-1} in the spectra of TMCHT was decreased progressively with corresponding increase at around 1470 cm^{-1}. Thus, the FTIR spectra of synthesized quaternized derivatives of CHT clearly reveal the introduction of methyl groups at nitrogen of glucosamine residues of CHT. When the quaternization was carried out at very high concentration of methyl iodide e.g. 15 fold excess (TMCHT3), another peak (weak) 686 cm^{-1} pertaining to methyl group is also noticed. A small peak appearing at around 1200 cm^{-1} in spectra of all TMCHT may be due to ether linkages. Therefore, the possibility of some methylation at hydroxyl group i.e. *O*-substitution cannot be obviated. Despite the usefulness of FTIR spectroscopy in characterization or qualitative analysis of TMCHT, its application to quantitative determination of DQ is limited due to lack of proportionality between the signals at 1470 cm^{-1} and the DQ.



CHT: Chitosan (Mol wt 135,839), TMCHT1 (CHT:CH_3I=1:5), TMCHT2 (CHT: CH_3I=1:10), TMCHT3 (CHT: CH_3I=1:15)

Figure 4.1 FTIR spectra of chitosan and trimethyl chitosan chloride

4.3.1.1.3 Conductometric titrations

Determination of degree of quaternization by conductometric titration [31] is based on the principle that when quaternized chitosan chloride e.g. TMCHT is treated with silver nitrate ($AgNO_3$) solution precipitates out silver chloride as shown by scheme 4.6.

Scheme 4.6 Reaction of TMCHT chloride with silver nitrate

Above scheme shows that one mole of silver nitrate reacts with equivalent amount of counter chloride ion (Cl^-) associated with one quaternized group of glucosamine residue. Thus, the reaction of one mole of silver nitrate with one chloride ion means the reaction with one quaternized group. This reaction, thus, can be employed for the determination of degree of quaternization (DQ) and the amount of $AgNO_3$ consumed can be determined by conductometric titrations.

Table 4.3 Effect of methyl iodide concentration on DQ: Conductometric titrations readings

$AgNO_3$ (0.1M)	Conductance (mMhos)								
	TMCHT1 CHT:CH_3I(1:5)			TMCHT2 CHT:CH_3I(1:10)			TMCHT3 CHT:CH_3I(1:15)		
	I	II	III	I	II	III	I	II	III
0	3.45	3.5	3.5	3.90	3.95	3.90	3.55	3.60	3.60
0.25	3.28	3.34	3.34	-	-	-	-	-	-
0.5	3.10	3.16	3.18	3.85	3.80	3.85	3.40	3.40	3.40
0.75	2.85	3.00	3.02	-	-	-	-	-	-
1.0	2.83	2.80	2.84	3.60	3.55	3.50	3.30	3.30	3.30
1.25	2.64	2.7	2.64	-	-	-	-	-	-
1.5	2.5	2.52	2.5	3.30	3.25	3.35	3.20	3.25	3.25
1.75	2.4	2.36	2.4	-	-	-	-	-	-
2.0	2.2	2.2	2.2	3.20	3.20	3.25	3.05	3.10	3.10
2.25	2.1	2.04	2.04	-	-	-	-	-	-
2.5	2.0	1.88	1.9	2.90	2.90	3.00	2.90	2.85	2.90
2.75	1.93	1.8	1.8	-	-	-	-	-	-
3.0	2.0	1.76	2.0	2.75	2.65	2.70	2.75	2.70	2.80
3.25	2.25	2.3	2.3	-	-	-	-	-	-
3.5	2.52	2..4	2.66	2.50	2.55	2.60	2.70	2.70	2.75
3.75	2.83	2.76	2.96	-	-	-	-	-	-
4.0	3.22	3.14	3.32	2.40	2.35	2.40	2.55	2.50	2.65
4.25	3.35	3.4	3.6	-	-	-	-	-	-
4.5	3.68	3.8	3.96	2.25	2.25	2.25	2.30	2.30	2.35
5.0	4.2	4.6	4.7	2.35	2.40	2.35	2.30	2.25	2.30
5.5	-	-	-	-	-	-	2.15	2.10	2.20
6.0	-	-	-	3.00	3.05	3.05	2.05	2.10	2.10
6.5	-	-	-	-	-	-	1.90	1.90	1.90
7.0	-	-	-	3.75	3.65	3.70	1.75	1.70	1.75
7.5	-	-	-	-	-	-	1.70	1.70	1.70
8.0	-	-	-	4.40	4.40	4.45	1.50	1.45	1.55
8.5	-	-	-	-	-	-	1.50	1.50	1.50
9.0	-	-	-	5.15	5.00	5.10	1.30	1.35	1.35
9.5	-	-	-	-	-	-	1.25	1.30	1.35
10.0	-	-	-	5.75	5.70	5.75	1.20	1.30	1.25
10.5	-	-	-	-	-	-	1.15	1.10	1.10
11.0	-	-	-	6.50	6.45	6.50	1.60	1.55	1.60
12.0	-	-	-	7.25	7.20	7.25	315	3.20	3.20
13.0	-	-	-	-	-	-	4.50	4.55	4.50
14.0	-	-	-	-	-	-	6.00	5.90	5.90

CHT: NaOH (1:2)

When a standard solution of silver nitrate (0.1M) is added into TMCHT solution, an equivalent amount of AgCl so formed is removed by precipitation resulting into the lowering of conductance. The burette reading at lowest conductance value gives the end point. The average degree of quaternization (DQ) can be calculated by using the expression 4.1.

$$\text{DQ (\%)} = \frac{M_Q \times V \times [AgNO_3]}{m} X100 \qquad \textbf{(4.1)}$$

Where,

M_Q is the molecular weight (g/mol) of repeating unit of TMCHT containing quaternized site, V and [$AgNO_3$] are the equivalent volume and concentration of $AgNO_3$ aqueous solution (0.1M) respectively, and m (g) is the mass of TMCHT.

As for illustration, the burette readings of 0.1M$AgNO_3$ and the corresponding conductance values for TMCHT1, 2 & 3 are presented in Table 4.3 and a representative titration curves shown in Figures 4.2, 4.3 and 4.4. The volume of 0.1M $AgNO_3$ required attaining lowest conductance for all the three TMCHT samples are given in Table 4.4.

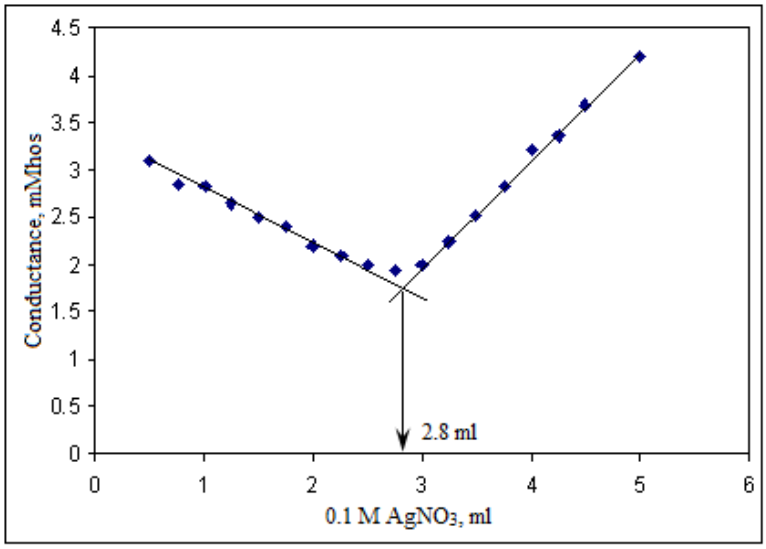


Figure 4.2 Conductometric titration of TMCHT1 *Vs* $AgNO_3$

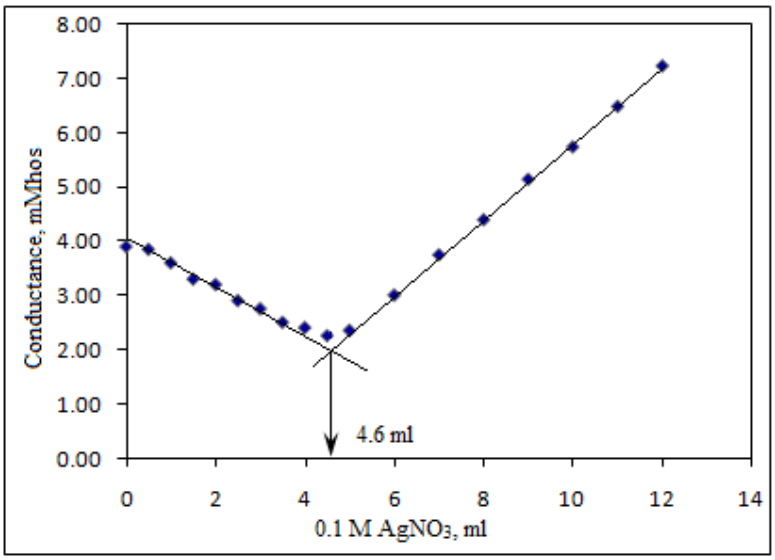


Figure 4.3 Conductometric titration of TMCHT2 *Vs* $AgNO_3$

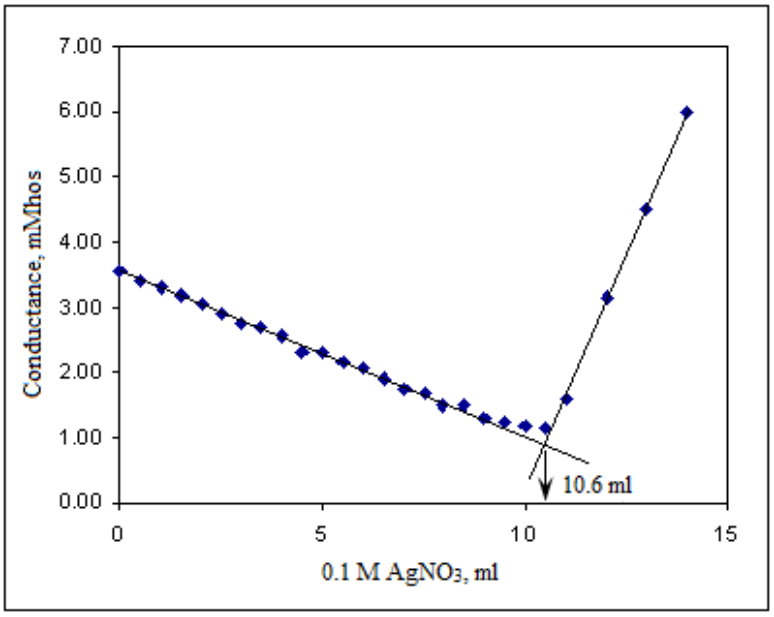


Figure 4.4 Conductometric titration of TMCHT3 *Vs* $AgNO_3$

Table 4.4 Conductometric method for determination of degree of quaternization (DQ) of TMCHT

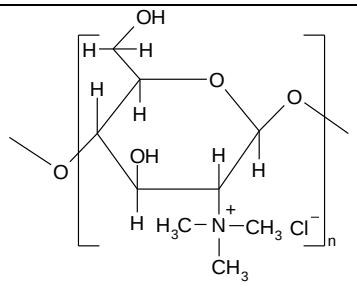
Sample	0.1 M $AgNO_3$ titrant (V), ml				Average (DQ), %
	I	II	III	Average	
TMCHT1	2.8	2.8	2.8	2.8	13.4
TMCHT2	4.6	4.8	4.4	4.6	22.0
TMCHT3	10.6	10.8	10.5	10.63	50.9

CHT: NaOH (1:2)

Calculations:

The degree of quaternization of TMCHT1 is determined as follows:

The molecular weight (M_Q) can be calculated from the glucosamine unit containing quaternized site.



C,9 X 12 =	108
O, 4 X 16 =	64
H, 18 X 1 =	18
N,1 X 14 =	14
Cl,1X 35.5=	35.5
Total, M_Q =	239.5

M_Q = 239.5, m= 0.5 g, [AgNO3] = 0.1M

B.R. = 2.8, 2.8, 2.8 = 2.8 ml i.e. V= 0.0028 L

Substituting these values in the expression 4.1,

$$DQ\ (\%) = \frac{239.5 \times 0.0028 \times 0.1}{0.5} X 100 = \mathbf{13.41\%}$$

Similarly, the DQ calculated for TMCHT2 and TMCHT3 are presented in Table 4.4

4.3.1.1.4 ^{1}HNMR spectroscopy

The average degree of quaternization of TMCHT is usually determined from the ratio between the intensity (I) of the signal (δ) due to quaternized amino site and the set

of signals attributed to anomeric hydrogen as a reference using the expression 4.6 [20, 31].

$$\text{Degree of Quaternization, DQ (\%)} = \frac{I_{QMe}}{9\left[I_{H1} + I_{H1'}\right]} X100 \qquad \textbf{(4.6)}$$

Where I_{QMe} is integral or intensity due to trimethyl group located at signal δ=3.1 to 3.3 ppm, and, I_{H1} and $I_{H'1}$ represent the integrals of the signals of H1 (the anomeric protons of the D-glucosamine units) and H1' (the anomeric protons of the N-acetyl D- glucosamine units) respectively, at peaks δ= 4.5 to 5.7 ppm. The ^{1}HNMR spectrum was determined for TMCHT3 is shown in Figure 4.5.

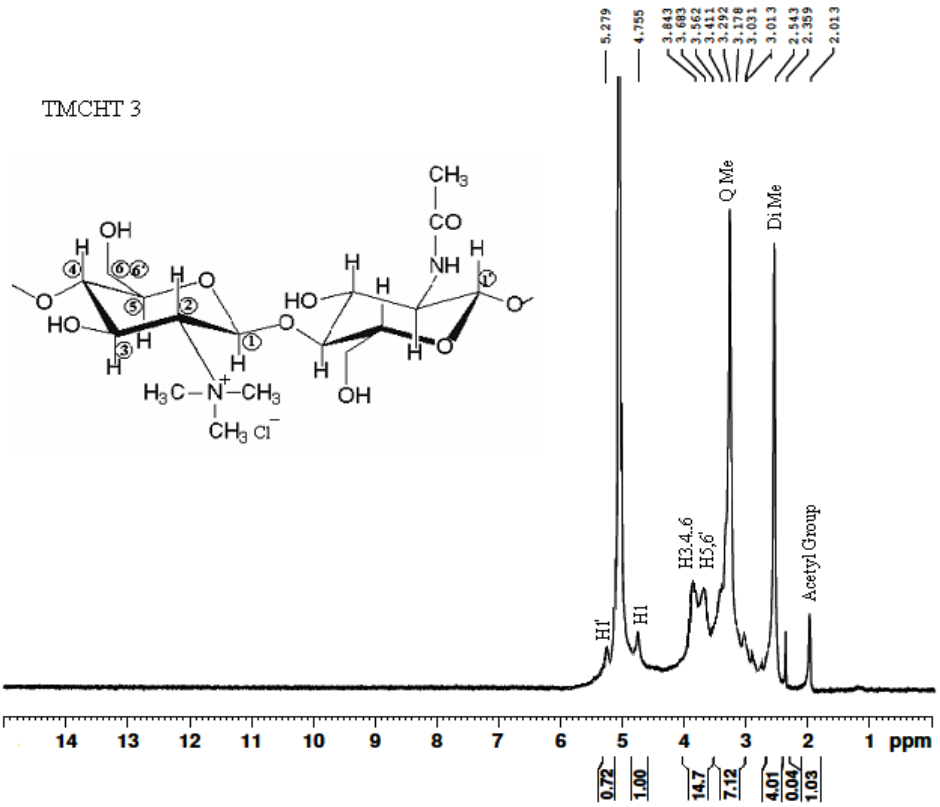


Figure 4.5 ^{1}H NMR spectrum of TMCHT 3

The spectrum indicates that trimethyl group is located at signal δ= 3.292 ppm and the integral was evaluated to be I_{QMe} = 7.12. The integral for anomeric proton H1 at δ= 4. 755 ppm was I_{H1}= 1, and that of H1' at δ= 5.279 ppm was found to be $I_{H1'}$= 0.72. The spectrum also shows dimethyl group at δ= 2. 543 ppm and the acetyl group at δ= 2.013 ppm with the corresponding signal intensities I_{DiMe}= 4.01 and I_{NAc}= 1.03.
Substituting the respective values in expression 4.6,

$$\text{DQ (\%)} = \frac{I_{QMe}}{9\left[I_{H1} + I_{H1'}\right]} X100 = \frac{7.12}{9\left[1+0.72\right]} X100 = \mathbf{46.0\ \%}$$

The DQ of TMCHT can also be precisely calculated with use of the expression 4.7 [31]. In this case, the denominator of the ratio will be increased as a consequence of the superimposition of signals but much less than in the previous case. In fact, the intensity due to hydrogen bonded to C2 will be added to those of the nine hydrogen atoms of three methyl groups of the quaternized site, six hydrogen atoms of two methyl groups of dimethylated sites and three hydrogen atoms of the methyl group of the acetamido moiety. Thus the impact of superimposition of signals for determination of degree of quaternization (DQ) is relatively much less important in this case.

$$\text{DQ (\%)} = \frac{I_{QMe}}{9} \times \frac{1}{S} \times 100 \qquad \textbf{(4.7)}$$

$$\text{S} = \frac{I_{QMe}}{9} + \frac{I_{DiMe}}{6} + \frac{I_{NAc}}{3} \qquad \textbf{(4.8)}$$

Where,
I_{QMe} and I_{DiMe} correspond, respectively, to the intensities of the signals due to quaternized and dimethylated nitrogen sites present in the chains of TMVRL and I_{NAc} is the signal intensity due to acetyl group. Thus, by computing the equations 4.7 and 4.8 using the integral values from spectrum,

$$S = \frac{I_{QMe}}{9} + \frac{I_{DiMe}}{6} + \frac{I_{NAc}}{3}$$

$$S = \frac{7.12}{9} + \frac{4.01}{6} + \frac{1.03}{3} = 1.8$$

$$DQ\ (\%) = \frac{I_{QMe}}{9} \times \frac{1}{S} \times 100$$

$$DQ\ (\%) = \frac{7.12}{9} \times \frac{1}{1.8} \times 100 = \mathbf{43.9\ \%}$$

These values of degree of quaternization obtained for TMCHT are in close agreement and therefore the average these two i.e. DQ = 44.5 % was taken for the consideration.

4.3.1.1.5 Elemental analysis

The elemental analysis for carbon, nitrogen, oxygen, hydrogen etc of chitosan and its derivatives can be a useful tool for the characterization i.e. for determination degree of deacetylation (DAC) of chitosan, degree of substitution (DS) by various alkyl and aryl groups or degree of quaternization (DQ) of quaternized chitosan. It is based on the principle that, proportional amount carbon content due to *N*-substitution on chitosan is increased without altering the nitrogen content provided the substituent is free of nitrogen. Thus by comparing the C/N of quaternized chitosan or *N*-substituted chitosan with that of parent chitosan the degree of substitution can be calculated. The expression 4.9 can be employed for such calculations [60].

$$\frac{C1}{N1} \times (1 - DS) + \frac{C2}{N2} \times DS = \frac{C3}{N3} DAC \qquad \textbf{(4.9)}$$

Where, C1/N1 is calculated from the formula of non substituted CHT i.e. glucosamine residue (GlcN), C2/N2 from the N-Substituted residue and C3/N3 is found value of sample by elemental analysis. DAC is degree of deacetylation per unit, which in our case was found to be 0.9.And, DS is degree of substitution of quaternization. The determination of degree of quaternization of TMCHT3 e.g. is illustrated as follows:

The C1/N1 calculated from the formula of non substituted CHT i.e. glucosamine residue (GlcN) is 5.14 and that for C2/N2 from the formula of TMCHT is 7.71. The CHN values of TMCHT3 found by elemental analysis were C3=44.63%, H3=7.07%, N3=6.28 and C3/N3 calculated was 7.11(Table 4.5). The determined C, H and N values of CHT and deferent *N*- modified chitosan derivatives are presented in Table 4.13.

Table 4.5 Calculations of different C/N ratios of TMCHT

<table>
<tr><td>$\frac{C1}{N1}$</td><td>Calculated from the formula of non substituted CHT i.e.GlcN residue</td><td>$\frac{C1}{N1}=\frac{6\times12}{1\times14}=\frac{72}{14}=5.14$</td></tr>
<tr><td>$\frac{C2}{N2}$</td><td>Calculated from the formula of N-Sub residue</td><td>$\frac{C2}{N2}=\frac{9\times12}{1\times14}=\frac{108}{14}=7.71$</td></tr>
<tr><td>$\frac{C3}{N3}$</td><td>Values of TMCHT 2 obtained by elemental analysis</td><td><table><tr><td>C3 (%)</td><td>H3 (%)</td><td>N3 (%)</td><td>C3/N3</td></tr><tr><td>40.19</td><td>7.04</td><td>6.42</td><td>6.26</td></tr></table></td></tr>
<tr><td>$\frac{C3}{N3}$</td><td>Values of TMCHT 3 obtained by elemental analysis</td><td><table><tr><td>C3 (%)</td><td>H3 (%)</td><td>N3 (%)</td><td>C3/N3</td></tr><tr><td>44.63</td><td>7.07</td><td>6.28</td><td>7.11</td></tr></table></td></tr>
</table>

Substituting these values in expression 4.9,

$$\frac{C1}{N1}\times(1-DS)+\frac{C2}{N2}\times DS=\frac{C3}{N3}DAC$$

TMCHT2

$$5.14\times(1-DS)+7.71\times DS=6.26\times0.9$$

DS = 0.1936 per unit OR **19.4 %**

TMCHT3

$$5.14\times(1-DS)+7.71\times DS=7.11\times0.9$$

DS = 0.4874 per unit OR **48.7 %**

The results for DQ of different TMCHT determined by various analytical methods namely conductometry, ^{1}HNMR and CHN analysis are presented in Table 4.6. It can be observed from the table that exactly same values for DQ are not obtained by different methods employed. Conductometry resulted higher values and somewhat nearer

to elemental analysis. The higher values obtained in conductometry may be attributed to the presence of loose chloride ions that remained with sample even after repeated purification. Further, the possibility of association of chloride ions with mono and di-substituted groups cannot be discarded. Regardless the higher values, the trend observed in conductometry were very much similar with results of elemental analysis.

Table 4.6 Comparative DQ values of TMCHT determined by various methods

Sample	DQ values (%) determined by:		
	Conductometry	^{1}HNMR	C/N Analysis
TMCHT1	13.4	-	-
TMCHT2	22.0	-	19.4
TMCHT3	50.9	44.5	48.7

4.3.1.1.6 Effect of reaction conditions on degree of quaternization of TMCHT

The success or the effectiveness of quaternization of chitosan is anticipated to be influenced by various reaction parameters such as methyl iodide concentration, reaction temperature, duration, process types (single or repeated treatments), and presence of alkali, electrolytes and solvents. The effect of concentration of methyl iodide can be seen from the Table 4.6. It was observed that the DQ increased progressively with increase in concentration of methyl iodide while all other parameters were constant. A sufficiently higher concentration of methyl iodide is always essential for such electrophilic substitution reactions to occur in heterogeneous medium. By increasing the reaction time or by repeated methylation process, increased DQ of chitosan has been reported earlier [19] but with the adverse effect on intrinsic viscosity and hence the molecular weight.

The mechanism of electrophilic substitution reaction proposed for the methylation of CHT in scheme 4.5 shows the indispensability of alkali in the reaction mixture. Accordingly, the effect of sodium hydroxide concentration on DQ of 1g CHT was studied. The methylation was carried out with methyl iodide (15 fold excess) and the caustic concentration was varied from zero concentration to 4 fold excess of CHT. The readings are given in Table 4.7, Table 4.8 and Table 4.9. The DQ was determined by conductometry are given in Table 4.10. These results reveal that the degree of

quaternization was almost nil in absence of alkali and then increased with increase in concentration of sodium hydroxide. Very high concentrations of sodium hydroxide, however, seemed to be detrimental on the quaternization efficiency. Further, incorporation of co-solvent such as NMP improved the degree of quaternization.

Table 4.7 Conductometric titration readings for TMCHT prepared in absence of sodium hydroxide

$AgNO_3$ (0.1M)	**Conductance, mMhos**		
	I	**II**	**III**
0	3.70	3.85	3.65
0.25	3.20	1.55	3.35
0.50	3.55	3.34	3.70
0.75	4.05	3.73	4.05
1.00	4.45	4.05	4.40
1.25	4.90	4.40	4.80
1.50	5.35	4.90	5.25
1.75	5.75	5.20	5.65
2.00	0.00	5.40	0.00
2.25	6.45	6.00	6.45
2.50	6.85	6.35	6.85

CHT: CH_3I=1:15, NMP 40ml

The poor quaternization yield in absence of alkali in quaternization reaction of chitosan can be explained on the fact that the CHT-Methyl cation intermediates formed during methylation (Scheme 4.5, step 1) liberate protons (H^+) as a by-product, as shown in scheme 4.7. The liberated protons being highly electrophilic in nature are captured by unshared electron pair of the nitrogen and thus stop the reaction at the amino site or preclude the forward reaction. Further, the low pH causes chain depolymerization due to glycoside bond cleavage, yielding low molecular weight derivatives [10]. These problems can be overcome by addition of strong bases that can remove the liberated H+ and favor the forward reaction. Different types of bases both organic (triethylamine) and inorganic (NaOH) can be employed in quaternization of CHT [61]. Studies have demonstrated that the inorganic bases were more efficient than organic bases due to their strong nucleophilic character. NaOH, for example, has a larger pKa than chitosan for

neutralizing the hydroiodic acid produced during the reaction and therefore avoids the protonation of the unreacted NH_2 groups [17].

Table 4.8 Effect of sodium hydroxide on DQ of TMCHT: Conductometric titrations readings

$AgNO_3$ (0.1M)	**Conductance (mMhos)**								
	CHT: NaOH (1:1) (With NMP)			**CHT: NaOH (1:2) (Without NMP)**			**CHT :NaOH (1:2) (With NMP)**		
	I	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**
0	3.80	3.80	3.80	3.70	3.60	3.70	3.55	3.60	3.60
0.5	3.75	3.65	3.70	3.60	3.60	3.65	3.40	3.40	3.40
1.0	3.60	3.50	3.50	3.50	3.40	3.40	3.30	3.30	3.30
1.5	3.40	3.35	3.50	3.25	3.25	3.30	3.20	3.25	3.25
2.0	3.25	3.20	3.20	3.20	3.20	3.25	3.05	3.10	3.10
2.5	3.00	3.00	3.00	3.10	3.10	3.10	2.90	2.85	2.90
3.0	2.80	2.90	2.90	2.90	2.85	2.85	2.75	2.70	2.80
3.5	2.60	2.70	2.60	2.80	2.75	2.75	2.70	2.70	2.75
4.0	2.50	2.55	2.55	2.75	2.75	2.65	2.55	2.50	2.65
4.5	2.30	2.35	2.30	2.50	2.55	2.55	2.30	2.30	2.35
5.0	2.10	2.15	2.20	2.45	2.50	2.50	2.30	2.25	2.30
5.5	1.90	1.85	1.90	2.40	2.35	2.35	2.15	2.10	2.20
6.0	1.80	1.85	1.85	2.25	2.30	2.30	2.05	2.10	2.10
6.5	1.60	1.65	1.65	2.30	2.25	2.30	1.90	1.90	1.90
7.0	1.40	1.45	1.50	2.25	2.20	2.20	1.75	1.70	1.75
7.5	1.35	1.30	1.35	2.35	2.35	2.35	1.70	1.70	1.70
8.0	1.30	1.35	1.30	2.75	2.80	2.75	1.50	1.45	1.55
8.5	1.45	1.50	1.55	3.50	3.50	3.50	1.50	1.50	1.50
9.0	2.00	2.05	2.05	2.40	2.35	2.35	1.30	1.35	1.35
9.5	-	-	-	-	-	-	1.25	1.30	1.35
10.0	3.05	3.00	3.00	4.25	4.20	4.20	1.20	1.30	1.25
10.5	-	-	-	-	-	-	1.15	1.10	1.10
11.0	3.95	4.00	4.00	5.25	5.20	5.25	1.60	1.55	1.60
12.0	5.00	4.90	4.90	6.15	6.20	6.15	315	3.20	3.20
13.0	6.15	6.00	6.20	6.60	6.65	6.65	4.50	4.55	4.50
14.0	6.80	6.80	6.85	7.00	6.90	6.90	6.00	5.90	5.90

CHT: CH_3I =1:15, NMP 40ml

Table 4.9 Effect of sodium hydroxide on DQ of TMCHT: Conductometric titrations readings

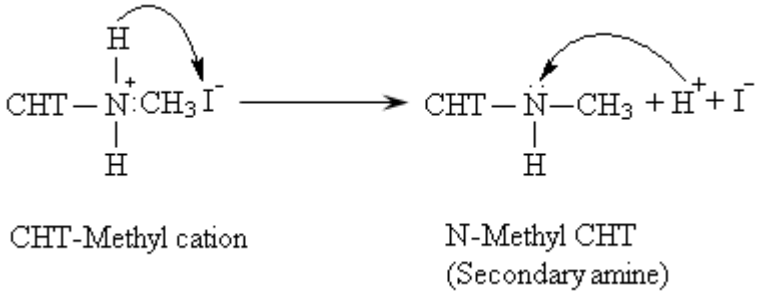
$AgNO_3$ (0.1M)	Conductance, mMhos					
	CHT: NaOH (1:3)			CHT: NaOH (1:4)		
	I	II	III	I	II	III
0	3.95	3.90	3.95	3.65	3.60	3.70
0.5	3.85	3.85	3.85	3.55	3.60	3.60
1.0	3.65	3.70	3.70	3.45	3.40	3.45
1.5	3.50	3.50	3.60	3.25	3.30	3.25
2.0	3.40	3.35	3.50	3.10	3.15	3.10
2.5	3.25	3.25	3.30	3.00	3.10	3.00
3.0	3.00	3.10	3.10	2.75	2.80	2.90
3.5	3.85	3.80	2.90	2.70	2.75	2.75
4.0	2.75	2.80	2.80	2.55	2.60	2.60
4.5	2.65	2.70	2.70	2.50	2.45	2.55
5.0	2.50	2.45	2.50	2.25	2.30	2.20
5.5	2.30	2.25	2.35	2.10	2.20	2.20
6.0	2.25	2.20	2.30	2.00	2.10	2.05
6.5	2.00	2.10	2.05	1.85	1.80	1.80
7.0	1.90	1.90	1.90	1.75	1.75	1.80
7.5	1.75	1.80	1.80	1.60	1.70	1.65
8.0	1.60	1.55	1.60	1.50	1.50	1.55
8.5	1.55	1.55	1.55	1.40	1.40	1.45
9.0	1.35	1.35	1.40	1.35	1.35	1.40
9.5	1.25	1.30	1.30	1.50	1.50	1.55
10.0	1.20	1.20	1.20	2.25	2.30	2.20
10.5	1.40	1.35	1.35	-	-	-
11.0	2.00	2.00	2.05	3.50	3.50	3.60
12.0	3.25	3.25	3.20	4.75	4.70	4.80
13.0	4.50	4.45	4.50	6.00	6.00	6.10
14.0	5.70	5.60	5.60	7.30	7.25	7.40
15.0	7.00	6.90	6.90	-	-	-
16.0	8.00	8.10	8.10	-	-	-

CHT: CH_3I=1:15, NMP 40ml

Table 4.10 Effect of sodium hydroxide on DQ of TMCHT

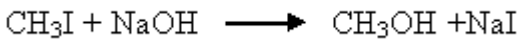
CHT: NaOH	$AgNO_3$(0.1M), ml				NMP, ml	DQ, %
	I	II	III	Average		
1:0	0.25	0.5	0.25	0.33	40	1.6
1:1	8.00	7.90	8.05	7.98	40	38.32
1:2	6.90	6.90	6.90	6.90	-	33.05
1:2	10.60	10.80	10.50	10.63	40	50.92
1:3	10.10	10.10	10.00	10.06	40	48.17
1:4	9.30	9.30	9.40	9.33	40	44.68

CHT: CH_3I =1:15



Scheme 4.7 Proton liberation step in methylation of CHT

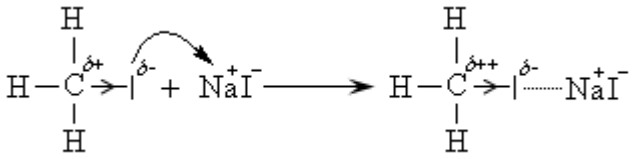
Higher concentrations of alkali, on the other hand, may lead to side reactions. The nucleophilic OH^- of the added NaOH can react with the electrophile (CH_3I) and produces alcohols (CH_3OH) as shown in scheme 4.8. Excessively higher concentrations of alkali may also lead to *O*-substitution to produce 3-*O*-methyl and 6-*O*-methyl derivatives [16, 62], which may cause steric hindrance for alkylation on amino groups. Overall effect will be lesser methylation on amino nitrogen.



Scheme 4.8 Side reaction due to alkali

The highly compact structure of chitosan due to extensive intramolecular and intermolecular hydrogen bonding between the chains confer it insolubility in neutral

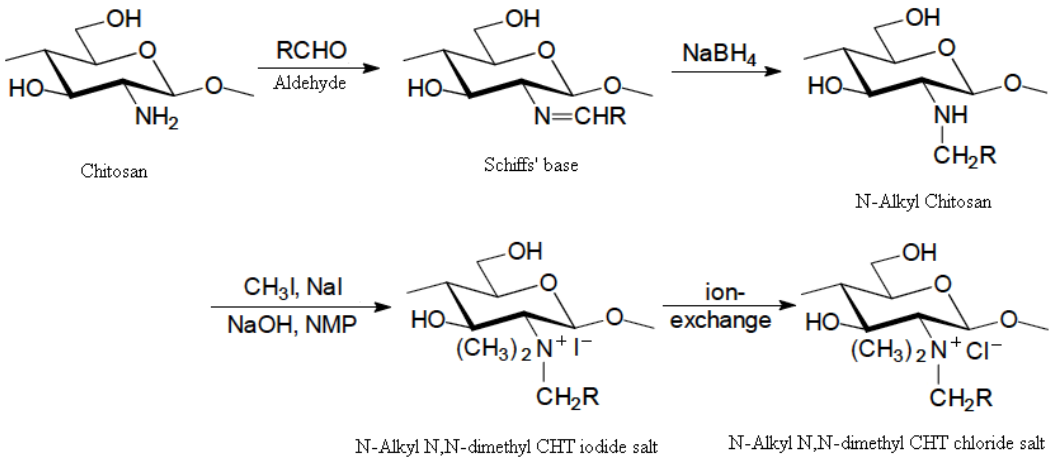
conditions. Since the quaternization reaction is performed in alkaline medium, the system is heterogeneous. This offers greater resistance for the penetration of methyl iodide and sodium hydroxide into the CHT structure and results into the poor degree of quaternization. Treatment of highly polar co-solvent such as *N*-methyl-2-pyrrolidone (other examples are DMF, DMSO etc) with CHT for an ample dwell time prior to the addition of methyl iodide and NaOH can swell and open up the CHT particles and facilitate the greater penetration alkylating chemicals [13]. The reaction speed and degree of methylation can also be increased by increasing temperature. However higher temperatures have been found to lead O-alkylation and also caused degradation of the chitosan as reported by Kotze et al [62]. Therefore, the same optimal temperature 50^0C and the sodium iodide concentration, as published elsewhere [31,37, 50], was adapted. Use of sodium iodide was reported to be necessary to adjust the overall concentration of reactants in the reaction medium [37]. It is believed that sodium iodide in reaction bath interacts with methyl iodide through ion- dipole forces and enhances the compatibility with the medium [22]. This interaction is also believed to make methyl carbon more electrophilic due to pulling of electronegative iodine of methyl iodide towards sodium ion of NaI and thus favor the methylation faster. The probable role of sodium iodide in methylation reaction is illustrated in scheme 4.9.



Scheme 4.9 Reaction of sodium iodide with methyl iodide

4.3.1.2 Synthesis of N-alkyl N, N-dimethyl chitosan chloride

In order to synthesize chitosan derivatives with quaternary ammonium salt having different methylene spacers a two step protocol was followed in which the first step involved synthesizing the *N*-alkyl derivatives of chitosan with varying degrees of hydrophobic character. In second step, these derivatives were subjected to quaternization to obtain targeted compounds.



Scheme 4.10 Synthesis *N*-alkyl *N*,*N*-dimethyl chitosan chloride

Table 4.11 Various ingredients used in the synthesis of *N*-sub CHT

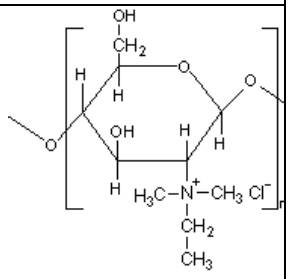
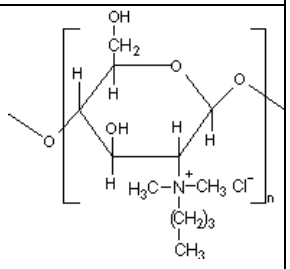
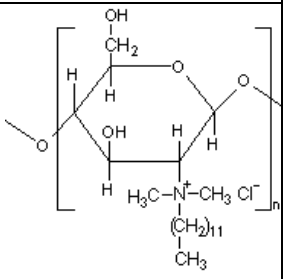
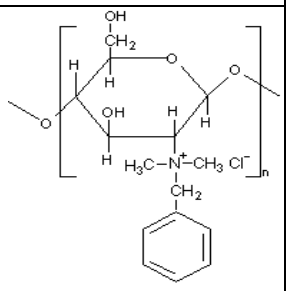
Sample	Aldehyde	*Aldehyde concentration		$NaBH_4$, g
		Relative to CHT	Quantity, g	
N-Et CHT(1:2)	Acetaldehyde	Two fold excess	0.6	1.0
N-Et CHT(1:4)	Acetaldehyde	Four fold excess	1.2	2.0
N-Bu CHT(1:2)	n-Butyraldehyde	Two fold excess	1.0	1.5
N-Bu CHT(1:4)	n-Butyraldehyde	Four fold excess	2.0	3.0
N-DodCHT(1:2)	Dodecyl Aldehyde	Two fold excess	2.4	3.6
N-DodCHT(1:4)	Dodecyl Aldehyde	Four fold excess	4.8	7.2
N-Bz CHT(1:2)	Benzaldehyde	Two fold excess	1.4	2.1
N-Bz CHT(1:4)	Benzaldehyde	Four fold excess	2.8	4.2
N-Np CHT(1:2)	1-Napthaldehyde	Two fold excess	2.0	3.0
N-Np CHT(1:4)	1-Napthaldehyde	Four fold excess	4.0	3.0

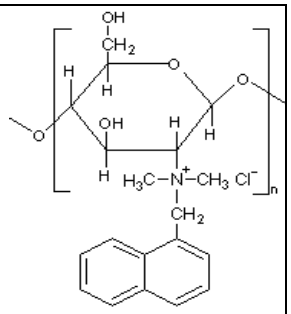
CHT 1 g, [**Conc calculated for aldehyde was based on molar conc in g. eq of -NH_2 of CHT. Calculation for two fold excess of acetaldehyde concentration can be illustrated as follows: 1g of CHT corresponds to 90 m.mol of NH_2 which in turn corresponds to 283 m.mol of acetaldehyde. That means 1g CHT contains 0.09 g eq of -NH_2 groups and reacts with acetaldehyde 0.283g (~ 0.3g). Therefore, for two fold excess, the quantity of pure acetaldehyde will be 0.3 X 2= 0.6 g.*]

Three alkyl groups of different chain length namely ethyl, butyl and dodecyl groups were, therefore, selected for the present study. These groups were introduced by reacting respective aldehyde, as listed in Table 4.11, with CHT in acidic medium to form Schiff's base. These intermediates were subjected to reductive amination known as Bosch reduction using sodium borohydride to produce *N*-alkyl derivatives. *N*-alkyl CHT

derivatives were further quaternized with methyl iodide as described in text for TMCHT (Scheme 4.10). The quaternization process for all these *N*-substituted CHT was carried out with methyl iodide of fifteen fold excess concentration. Different grades of *N*-alkyl CHT and *N*-alkyl *N, N*-dimethyl chitosan chloride derivatives synthesized for textile application are listed in Table 4.12.

Table 4.12 Various *N*-substituted CHT derivatives

Code	**Chemical Name**	**Structure of quaternized derivative**
N-Et CHT(1:2)	N-Ethyl Chitosan (1:2)	
N-Et CHT(1:4)	N-Ethyl Chitosan (1:4)	
N-Et Q CHT(1:2)	N-Ethyl N,N Dimethyl Chitosan (1:2) Chloride	
N-Et Q CHT(1:4)	N-Ethyl N,N Dimethyl Chitosan (1:4) Chloride	
N-Bu CHT(1:2)	N-Butyl Chitosan (1:2)	
N-Bu CHT(1:4)	N-Butyl Chitosan (1:4)	
N-Bu Q.CHT(1:2)	N-Butyl N,N Dimethyl Chitosan (1:2) Chloride	
N-Bu Q.CHT(1:4)	N-Butyl N,N Dimethyl Chitosan (1:4) Chloride	
N-DodCHT(1:2)	N-Dodecyl Chitosan (1:2)	
N-DodCHT(1:4)	N-Dodecyl Chitosan (1:4)	
N-DodQ.CHT(1:2)	N- Dodecyl N,N Dimethyl Chitosan (1:2) Chloride	
N-DodQ.CHT(1:4)	N- Dodecyl N,N Dimethyl Chitosan (1:4) Chloride	
N-Bz CHT(1:2)	N-Benzyl Chitosan (1:2)	
N-Bz CHT(1:4)	N-Benzyl Chitosan (1:4)	
N-Bz Q.CHT(1:2)	N-Benzyl N,N Dimethyl Chitosan (1:2) Chloride	
N-Bz Q.CHT(1:4)	N-Benzyl N,N Dimethyl Chitosan (1:4) Chloride	

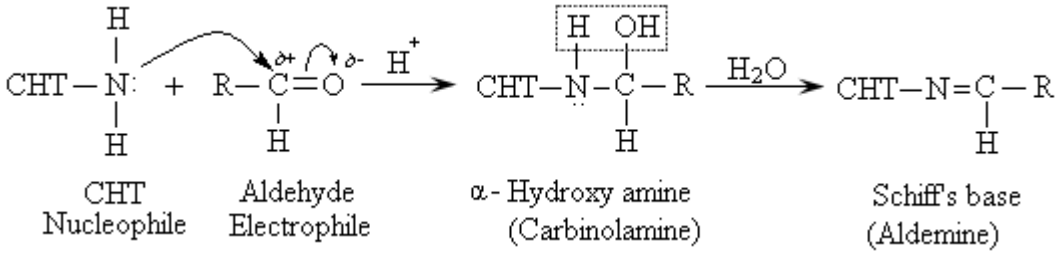
N-Np CHT(1:2)	N-(1-Naphthyl) Methylene Chitosan (1:2)	
N-Np CHT(1:4)	N-(1-Naphthyl) Methylene Chitosan (1:4)	
N-Np Q.CHT(1:2)	N-(1-Naphthyl) Methylene N,N Dimethyl Chitosan (1:2) Chloride	
N-Np Q.CHT(1:4)	N-(1-Naphthyl) Methylene N,N Dimethyl Chitosan (1:4) Chloride	

CHT: CH_3I =1:15, Values in parenthesis indicate CHT: Aldehyde ratio

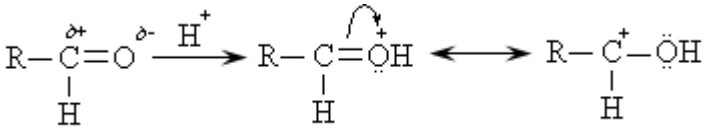
4.3.1.2.1 Reaction mechanism

The primary amines of chitosan (CHT) readily add to the carbonyl group (>C=O) of aldehydes to form α- hydroxy amines, also called carbinolamines. These species undergo spontaneous elimination of water molecule to yield imines or Schiff's base [22]. This is an electrophilic substitution reaction and follows S_N2 mechanism. The carbon-oxygen bond in carbonyl group of aldehydes is highly polarized due to the presence of electro-ve oxygen. The electrons constituting the π bonds are partially shifted towards oxygen as a result of electromeric effect. It implies that the carbon atom of carbonyl group is electron deficient i.e. electrophile and therefore readily attacks nucleophilic amino group of CHT.

The acidic pH in this reaction serves two purposes. Firstly, it promotes the dissolution of chitosan conferring the homogeneity to the reaction medium. Secondly, it acts as a catalyst. The proton released by the acid combines with the carbonyl oxygen and thus attenuates the electron deficiency of the carbon atom and thus the attack of nucleophile is enhanced. The various steps of the reaction mechanism are shown in scheme 4.11.

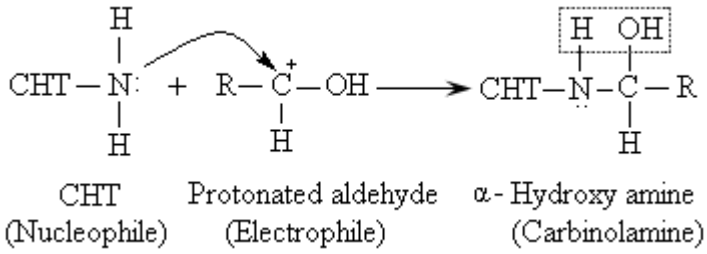


(1)

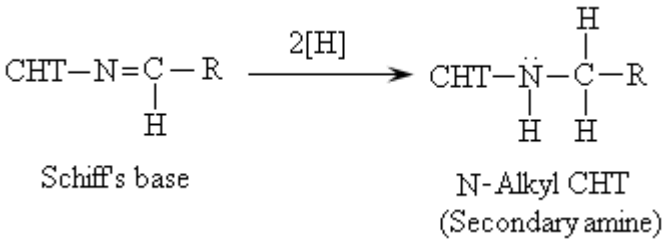


(2)

Acid catalyzed reaction , protonation of aldehyde



(3)



(4)

Reduction of Schiff's base (Bosch reduction)

Scheme 4.11 Electrophilic substitution reaction: methylation of CHT

4.3.1.2.2 FTIR spectroscopy of N-alkylated chitosans

The FTIR spectra of different *N*-alkylated and quaternized *N*-alkylated chitosan are presented in Figures 4.6, 4.7 and 4.8. The FTIR spectrum of N-ethyl chitosan (Figures 4.6) shows a reduction in broad band at 3372 cm^{-1} that indicates the removal of some of H from NH_2. A characteristic peak at wavenumber 2928 cm^{-1} arised is mainly due to C-H stretching due to the introduction of methylene group. The intensities of these peaks were found to be increased with increase in methylene spacer as is observed in Figures 4.7 and 4.8. The terminal methyl group of attached ethyl chain is also recognized by a weak absorption peak at 1457 cm^{-1} due to C-H bending vibrations. Although marked differences were not observed in FTIR spectra for the quaternized chitosan, the intensity at peak around 1457 cm^{-1} was found to be increased which is the characteristic peak of methyl group [16, 23].

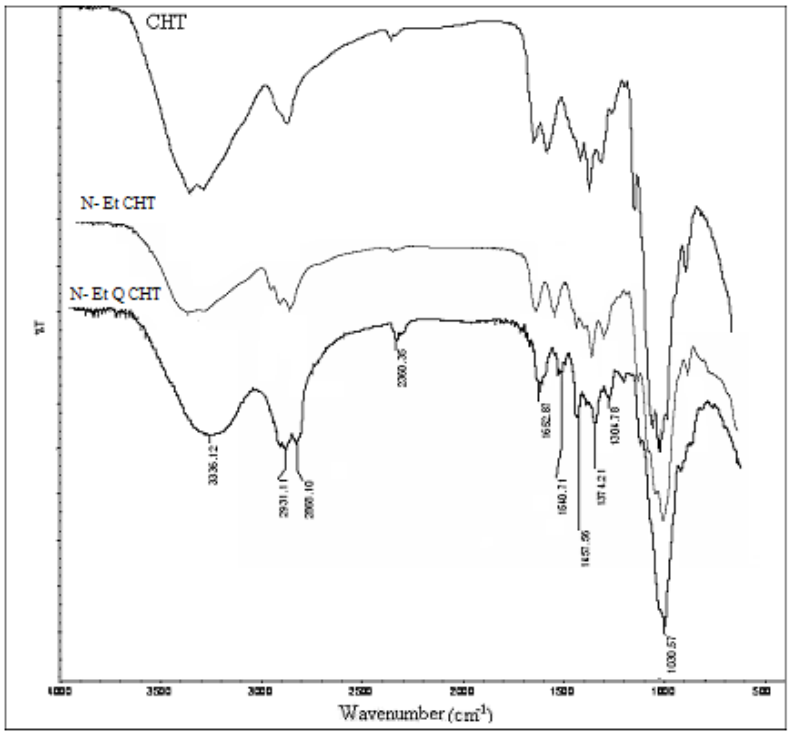


Figure 4.6 FTIR spectra of *N*- ethyl chitosan derivatives

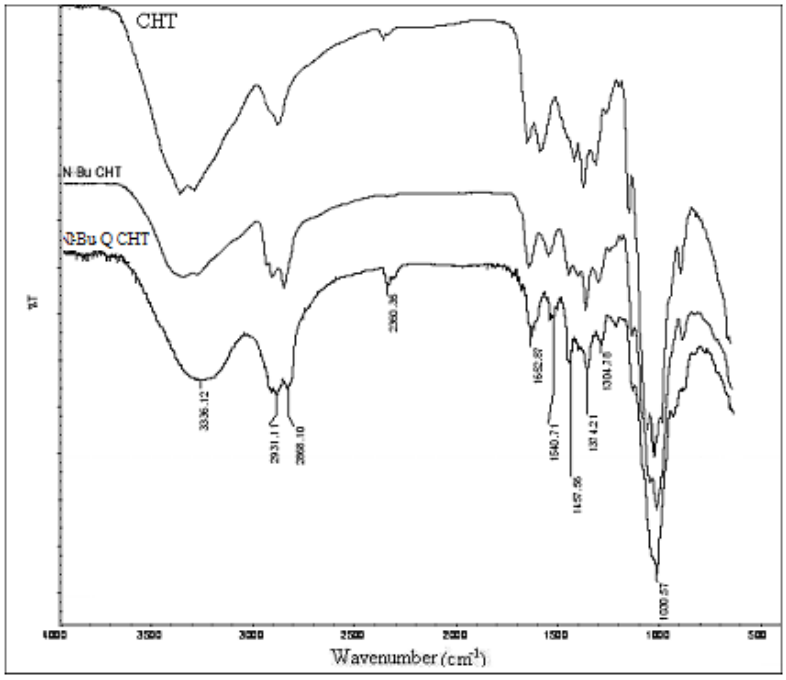


Figure 4.7 FTIR spectra of *N*-butyl chitosan derivatives

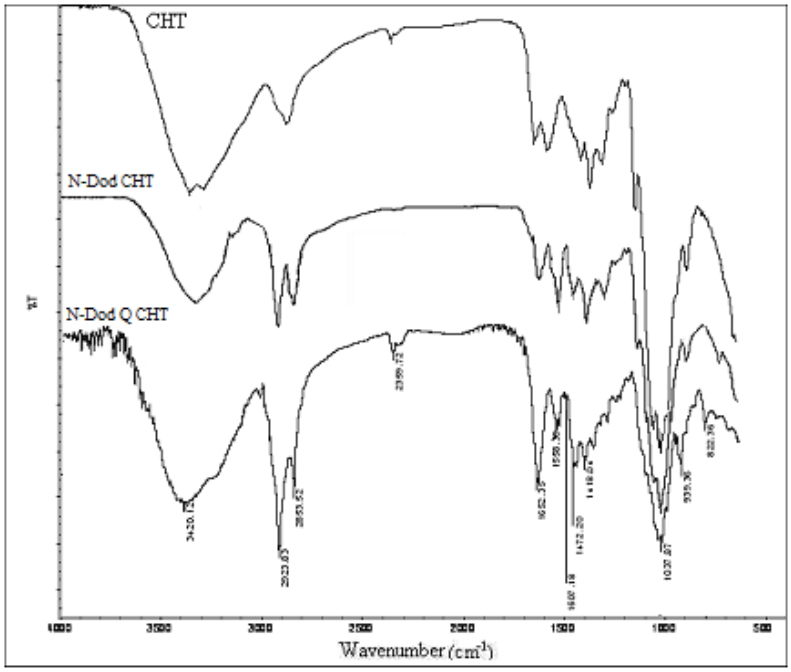


Figure 4.8 FTIR spectra of *N*-dodecyl chitosan derivatives

4.3.1.2.3 Analysis of ^{1}HNMR spectra of N-alkylated chitosans

The ^{1}HNMR spectroscopy was performed for the quantitative determination of degree of substitution (DS) and degree of quaternization (DQ) of synthesized *N*-alkyl CHT and their quaternized derivatives. The degree of substitution from the ^{1}HNMR spectrum can be calculated from the ratio of intensities produced due to proton vibration / resonance from C-H bond of substituent to that of either C2 proton or the sum of anomeric protons. In present study, the degree of substitution (DS) was calculated using two different equations 4.10 [28] and 4.11 [24, 25] and the average of these two results was considered. The spectra of these derivatives are shown in Figures 4.9 to 4.14. The values of these parameters determined for *N*-alkyl CHT and their quaternized derivatives are presented in Table 4.19. The ^{1}H-NMR spectrum of modified chitosan displays broadening of the characteristic peaks at signals in the 1.7-0.9 ppm region, attributed to the protons of the methyl (-CH_3) and methylene (-CH2-) groups grafted onto the chitosan chain, which evidences the chemical modifications resulting from the alkylation reaction. The broad multiplet peaks from 1.3 to 1.7 ppm are attributed to the methylene hydrogen of the -CH_2- groups, while a typical peak at 0.9 ppm corresponds to the methyl protons at the terminal groups -CH_3, both belonging to the -C_2H_5 aliphatic chain [13, 63- 65]. The

degree of quaternization of the quaternized *N*-alkylated samples was determined using the equation 4.6 with little modification.

[1]NMR spectrum analysis of N- ethyl chitosan [N- Et CHT (1:2)]

The [1]HNMR spectrum of the *N*-Et CHT (1:2) prepared from two fold excess of acetaldehyde is shown in Figure 4.9. In the figure, the peak at δ= 1.019 ppm is attributed to terminal methyl group of pendant ethyl chain and the integral is $I_{Me\ (T)}$ = 2.82 and the signal at δ= 1.323 ppm is assigned to -CH2- of ethyl chain with integral $I_{(-CH2-)}$ = 1.47. This figure also depicts the acetyl group at δ= 1.960 with integral I_{NAc}= 1.0, and protons at C2,3,4,5,6 & 6' between range of δ= 3 to 4 ppm with total intensity $I_{H3\text{-}6,6'}$ = 7.22 . The C2 proton was traced at peak $\delta_{(H2)}$ = 2.854 with integral the I_{H2} = 3.78. The anomeric protons H1 and H1' are traced at δ= 4.601ppm and δ= 5.433 ppm respectively and the corresponding integrals are found to be I_{H1}= 1 and $I_{H1'}$= 0.66.

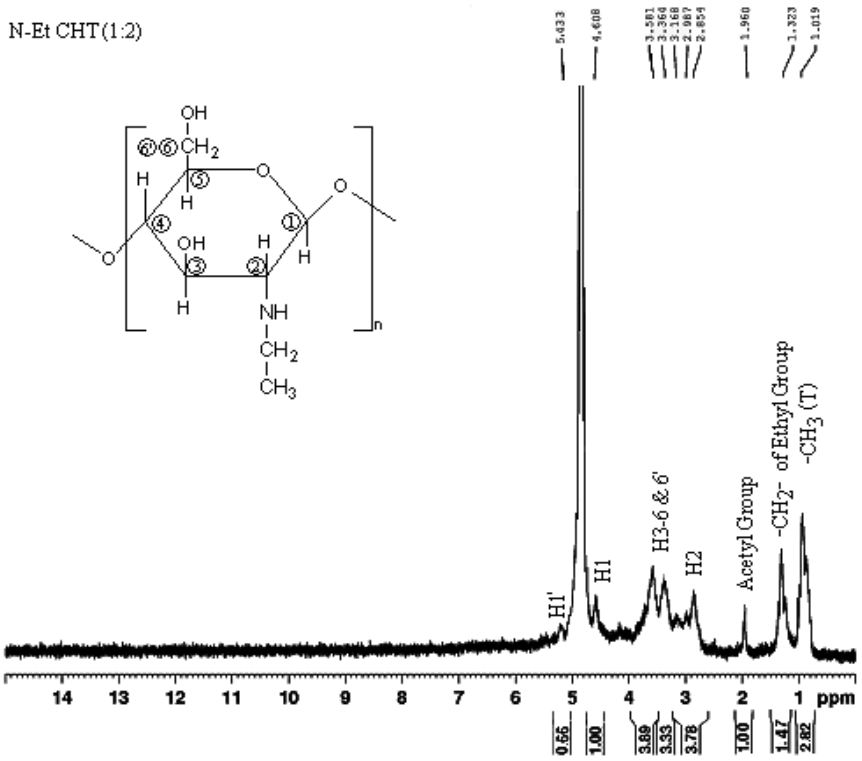


Figure 4.9 [1]HNMR spectrum of N-Ethyl chitosan (1:2)

Calculations:

Method1: The degree of substitution (DS, %) can be calculated by substituting the values of integrals in equation 4.10

$$DS(\%) = \frac{I_{(-CH2-)}}{2\left[I_{H1} + I_{H1'}\right]} X100 \qquad \textbf{(4.10)}$$

$$= \frac{1.47}{2\left[1+0.66\right]} X100 = \textbf{44.3 \%}$$

Method 2:

$$\frac{nDS}{6} = \frac{A}{\left[B+C\right]} \quad \textbf{OR} \quad \frac{nDS}{6} = \frac{I_{Et}}{\left[I_{H2} + I_{H3-6,6'}\right]} \qquad \textbf{(4.11)}$$

Where, A = Peak area of substituent.

Therefore, A= I_{Et} = I_{Me} + I_{-CH2-} = 2.82 +1.47 = 4.29

B = Peak area of H2 (proton at C2) of glucosamine residue (Glc N).

i.e. B = I_{H2} = 3.78 at δ= 2.854ppm for proton at C2 of GlcN.

C = Peak area of protons bounded to C-3,4,5,6& 6' of GlcN.

C = $I_{H3\text{-}6\&6'}$ = 3.33+ 3.89 =7.22 (at δ= 3.168 and 3.581ppm)

n= Number of proton per substituent -CH_2-CH_3 = 5

The denominator '6' at LHS is the total number of protons bound to C2 of GlcN and C3-6&6' ie.[B+C] or [H2+ H3,4,5,6& 6'].

By substituting above values in equation **4.11,**

$$DS = \frac{6 \times 7.49}{5 \times \left[3.78 + 3.33 + 3.89\right]} = 0.468 \text{ ethyl groups/glucosamine unit.}$$

DS (%) = 46.8 %

Average of method 1 and method 2, **DS = 45.5 %**

[1]NMR Spectrum Analysis of N- Ethyl N, N-dimethyl chitosan chloride (1:2) [N-Et Q CHT(1:2)]

The [1]HNMR spectrum of N- Ethyl N, N-dimethyl chitosan chloride (1:2) [N-Et Q CHT(1:2)] is shown in Figure 4.10.

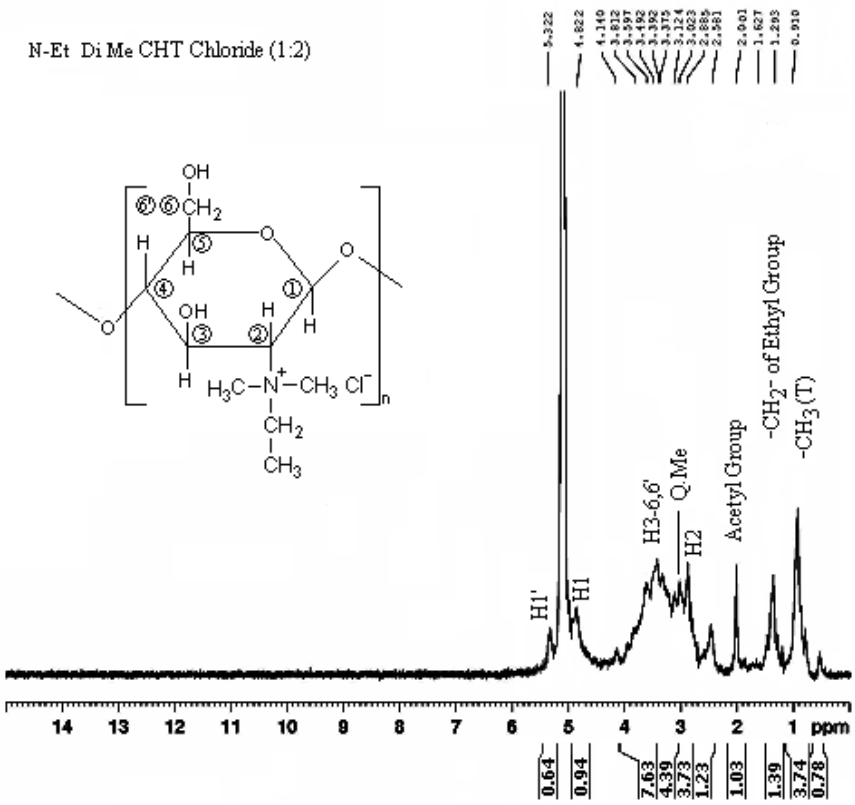


Figure 4.10 [1]HNMR spectrum of *N*- ethyl *N, N*-dimethyl chitosan chloride (1:2)

Various peaks and their intensities depicted by [1]HNMR of N-QEtCHT (1:2) and the determined DQ are summarized below.

$I_{Me(T)}$ =3.74	$\delta_{Me(t)}$= 0.9201	Three protons (3H) of terminal methyl of ethyl chain.
I_{Et} =	$\delta_{(CH2)}$ = 1.293	2 protons (2H) of 1 methylene group of ethyl chain
$I_{(CH2)}$ = 1.39		
n = 5		5 protons ethyl group [-C**H**$_2$-C**H**$_3$]

I_{NAc} = 1.0	$\delta_{(NAc)}$ =2.001	Three protons (3H) methyl terminal of acetyl group. -N-CO-C**H$_3$**
I_{H2} = 3.73	$\delta_{(H2)}$ = 2.885	One proton (1H) bound to C2 glucosamine (GlcN) residue.
$I_{H3\text{-}6,6'}$ = 7.63	$\delta_{(H3\text{-}6,6')}$ = 3.2-4.5	Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN.
I_{QMe}= 4.39	$\delta_{(QMe)}$ =3.124	Six protons (6H) of two methyl groups attached to N-ethyll substituted of GlcN residue.
I_{DiMe}= 1.23	$\delta_{(DiMe)}$ =2.581	Six protons (6H) of two methyl groups attached to free amino groups of GlcN residue.
I_{H1} = 0.94	$\delta_{(H1)}$ = 4.432	One anomeric proton (1H) of the glucosamine units
$I_{H1'}$ = 0.64	$\delta_{(H1)}$ = 5.422	One anomeric proton (1H) of the N-acetyl glucosamine units
I= 0.18	δ = 0.78	

DS = 45.5 %

From these data, the degree of quaternization (DQ, %) is calculated by using the equation 4.12 as follows.

$$DQ\ (\%) = \frac{I_{QMe}}{6\left[I_{H1} + I_{H1'}\right]} X100 \qquad \textbf{(4.12)}$$

$$= \frac{4.39}{6\left[0.94 + 0.64\right]} X100 = \textbf{46.3 \%}$$

The digit '6' at the denominator of right hand side is the number of protons of two methyl groups attached to ethyl substituted N of GlcN residue.

N- Ethyl chitosan [N- Et CHT (1:4])

Various peaks (δ) with corresponding integrals (I) for N-Et CHT (1:4) (Figure not shown) and the determined DS values using the equations 4.10 and 4.11 are presented as follows:

$\delta_{Me(t)}$= 0.954ppm	$I_{Me(T)}$ = 4.67	Three protons (3H) of terminal methyl of ethyl chain.
$\delta_{(CH2)}$ = 1.323 ppm	I_{Et} = $I_{(CH2)}$ = 2.82	2 protons (2H) of one methylene group of ethyl chain
n = 5		5 protons ethyl group [-C**H$_2$**-C**H$_3$**]
$\delta_{(NAc)}$ =1.947 ppm	I_{NAc} = 1.07	Three protons (3H) methyl terminal of acetyl group -N-CO-C**H$_3$**
$\delta_{(H2)}$ = 2.854 ppm	I_{H2} = 1.78	One proton (1H) bound to C2 glucosamine (GlcN) residue.
$\delta_{(H3\text{-}6,6')}$ = 3.2-4.5 ppm	$I_{H3\text{-}6,6'}$ = 3.33+3.89 =2.22	Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN.
$\delta_{(H1)}$ = 4.601 ppm	I_{H1} = 1.00	One anomeric proton (1H)of the glucosamine units
$\delta_{(H1)}$ = 5.174 ppm	$I_{H1'}$ = 0.69	One anomeric proton (1H) of the N-acetyl glucosamine units

DS = Method1: 83.47%, Method 2: 81.71%, Average DS = **82.6 %**

^{1}NMR Spectrum analysis of N- butyl chitosan [N- Bu CHT (1:2)]

The ^{1}HNMR spectrum of the *N*-Bu CHT (1:2) is shown in Figure 4.11.

Various peaks (δ) with corresponding integrals (I) for N-Bu CHT (1:2) depicted by ^{1}HNMR spectrum and the DS (%) evaluated using equations 4.10 and 4.11 are presented below.

$\delta_{Me(t)}$= 0.968ppm	$I_{Me(T)}$ = 2.03	Three protons (3H) of terminal methyl of butyl chain.
$\delta_{(CH2)}$ =1.376ppm	I_{Bu} =$I_{(CH2)3}$- = 2.60	6 protons (6H) of three methylene group of butyl chain
n = 9		9 protons butyl group [- (C**H$_2$**)$_3$-C**H$_3$**]
$\delta_{(NAc)}$ =2.081ppm	I_{NAc} = 1.0	Three protons (3H) methyl terminal of acetyl group. -N-CO-C**H$_3$**

$\delta_{(H2)}$ = 3.008ppm	I_{H2} = 1.74	One proton (1H) bound to C2 glucosamine (GlcN) residue.
$\delta_{(H3\text{-}6,6')}$ = 3.1-4.2 ppm	$I_{H3\text{-}6,6'}$ = 5.75	Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN.
$\delta_{(H1)}$ = 4.588ppm	I_{H1} = 0.63	One anomeric proton (1H) of the glucosamine units
$\delta_{(H1)}$ = 5.533ppm	$I_{H1'}$ = 0.48	One anomeric proton (1H) of the N-acetyl glucosamine units

D.S. = 39.04, 41.21, Average **DS = 40.1 %**

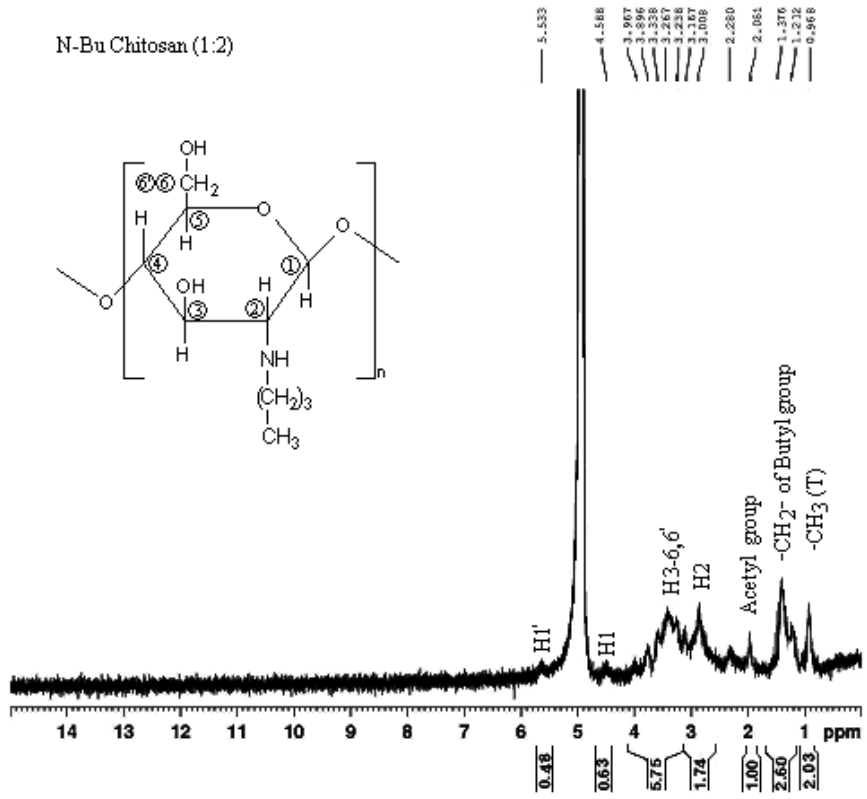


Figure 4.11 ^{1}HNMR spectrum of *N*-butyl chitosan (1:2)

^{1}NMR Spectrum analysis of N- Butyl N, N-dimethyl chitosan chloride (1:2) [N-Bu Q CHT(1:2)]

The H^{1}NMR spectrum of N Butyl N,N dimethyl chitosan chloride is shown in Figure 4.12.

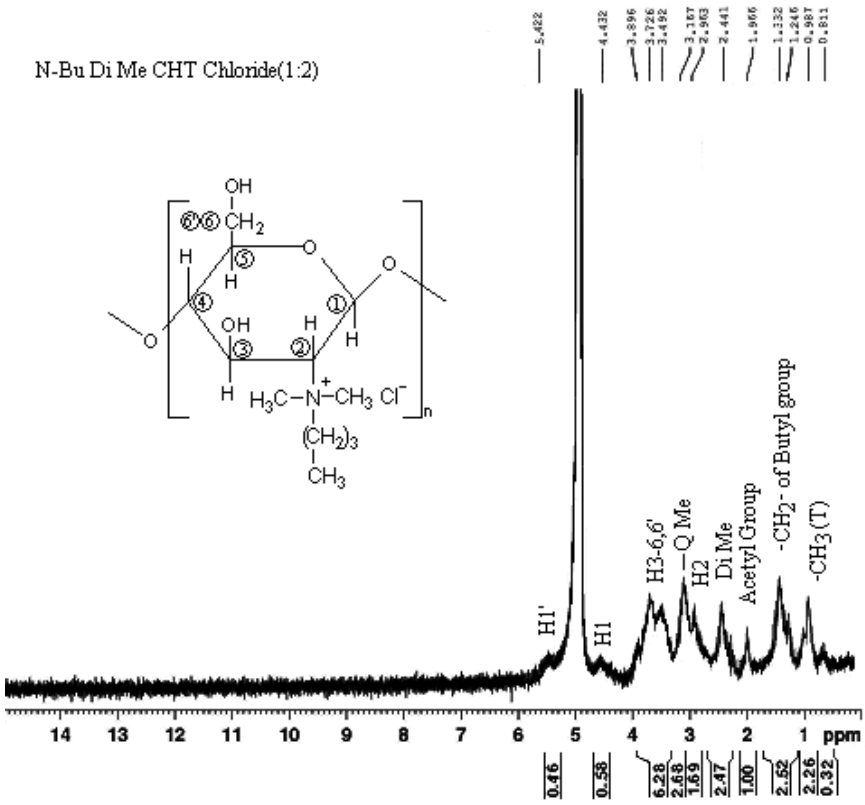


Figure 4.12 [1]HNMR spectrum of *N*-butyl *N, N*-dimethyl chitosan chloride (1:2)

Various peaks (δ) with corresponding integrals (I) for N-Bu Q CHT (1:2) depicted by [1]HNMR spectrum and the DQ determined using equation 4.12 are summarized as below.

$\delta_{Me(t)}$= 0.987 ppm	$I_{Me(T)}$ =2.26	Three protons (3H) of terminal methyl of ethyl chain.
$\delta_{(CH2)3}$ = 1.332ppm	I_{Bu} = $I_{(CH2)3}$ = 2.52	6 protons (6H) of three methylene group of butyl chain
n = 9		9 protons butyl group [- (C**H**$_2$)$_3$-C**H**$_3$]
$\delta_{(NAc)}$ =1.966 ppm	I_{NAc} = 1.0	Three protons (3H) methyl terminal of acetyl group -N-CO-C**H**$_3$
$\delta_{(H2)}$ = 2.893 ppm	I_{H2} = 1.69	One proton (1H) bound to C2 glucosamine (GlcN) residue.
$\delta_{(H3\text{-}6,6')}$ = 3.2-4.2 ppm	$I_{H3\text{-}6,6'}$ = 6.28	Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN.

$\delta_{(QMe)}$ =3.108 ppm	I_{QMe}= 2.68	Six protons (6H) of two methyl groups attached to N- butyl substituted of GlcN residue.
$\delta_{(DiMe)}$ =2.411 ppm	I_{DiMe}= 2.47	Six protons (6H) of two methyl groups attached to free amino groups of GlcN residue.
$\delta_{(H1)}$ = 4.432 ppm	I_{H1} = 0.58	One anomeric proton (1H) of the glucosamine units
$\delta_{(H1')}$ = 5.422 ppm	$I_{H1'}$ = 0.46	One anomeric proton (1H) of the N-acetyl glucosamine units
δ = 0.811 ppm	I= 0.32	

DS (%) =40.1 %

DQ (%) =42.9 %

[1]NMR spectrum analysis of N- butyl chitosan [N- Bu CHT (1:4)]

Various peaks (δ) with corresponding integrals (I) for N-BuCHT(1:4) depicted by ^{1}HNMR spectrum (figure not shown) and the DS determined using equations 4.10 and 4.11 are summarized as below.

$\delta_{Me(t)}$= 0.921ppm	$I_{Me(T)}$ = 1.80	Three protons (3H) of terminal methyl of ethyl chain.
$\delta_{(CH2)}$ =1.476, 1.322 ppm	I_{Bu} = $I_{(CH2)3}$ = 3.82	6 protons (6H) of three methylene group of butyl chain
	n = 9	9 protons butyl group,-(C$\mathbf{H_2}$)$_3$-C$\mathbf{H_3}$
$\delta_{(NAc)}$ =1.962 ppm	I_{NAc} = 0.78	Three protons (3H) methyl terminal of acetyl group, -N-CO-C$\mathbf{H_3}$
$\delta_{(H2)}$ = 2.960 ppm	I_{H2} = 1.67	One proton (1H) bound to C2 glucosamine (GlcN) residue.
$\delta_{(H3\text{-}6,6')}$ = 3.2-4.5 ppm	$I_{H3\text{-}6,6'}$ = 3.70	Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN.
$\delta_{(H1)}$ = 4.551 ppm	I_{H1} = 0.52	One anomeric proton (1H)of the glucosamine units
$\delta_{(H1)}$ = 5.614 ppm	$I_{H1'}$ = 0.38	One anomeric proton (1H) of the N-acetyl glucosamine units

D.S. = 71.85 & 70.52% , Average **DS = 71.2 %**

[1]NMR spectrum analysis of N- dodecyl chitosan (1:2) [N- DodCHT(1:2)]

Various peaks (δ) with corresponding integrals (I) for N-DodCHT (1:2) depicted by ^{1}HNMR spectrum (figure not shown) and the DS determined using equations 4.10 and 4.11 are summarized as below.

$\delta_{Me(t)}$= 0.903ppm	$I_{Me(T)}$ = 1.52	Three protons (3H) of terminal methyl of dodecyl chain.
$\delta_{(CH2)}$ =1.376ppm	I_{Dod} = $I_{(CH2)11}$=2.44	22 protons (22H) of 11 methylene groups of dodecyl chain
n = 25		25 protons dodecyl group [- (CH_2)$_{11}$-CH_3]
$\delta_{(NAc)}$ =2.011ppm	I_{NAc} = 1.0	Three protons (3H) methyl terminal of acetyl group. -N-CO-CH_3
$\delta_{(H2)}$ = 3.061 ppm	I_{H2} = 1.49	One proton (1H) bound to C2 glucosamine (GlcN) residue.
$\delta_{(H3\text{-}6,6')}$ = 3.2-4.5 ppm	$I_{H3\text{-}6,6'}$ = 3.00	Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN.
$\delta_{(H1)}$ = 4.638 ppm	I_{H1} = 0.31	One anomeric proton (1H)of the glucosamine units
$\delta_{(H1')}$ = 5.403 ppm	$I_{H1'}$ = 0.17	One anomeric proton (1H) of the N-acetyl glucosamine units

DS = 23.11% & 21.16%, Average DS = 22.1 %

[1]NMR spectrum analysis of N- dodecyl chitosan [N- DodCHT (1:4)]

The ^{1}HNMR spectrum of N- dodecyl chitosan is shown in Figure 4.13.

Various peaks (δ) with corresponding integrals (I) for N-DodCHT (1:4) depicted by ^{1}HNMR spectrum and the DS determined using equations 4.10 and 4.11 are summarized as below.

$\delta_{Me(t)}$= 0.912ppm	$I_{Me(T)}$ = 2.56	Three protons (3H) of terminal methyl of dodecyl chain.

$\delta_{(CH2)}$ =1.413ppm	I_{Dod} = $I_{(CH2)11-}$ = 4.69	22 protons (22H) of three methylene group of dodecyl chain
n = 25		25 protons dodecyl group,-(C**H**$_2$)$_{11}$-C**H**$_3$
$\delta_{(NAc)}$ =2.000 ppm	I_{NAc} = 1.0	Three protons (3H) methyl terminal of acetyl group, -N-CO-C**H**$_3$
$\delta_{(H2)}$ = 2.919 ppm	I_{H2} = 1.68	One proton (1H) bound to C2 glucosamine (GlcN) residue.
$\delta_{(H3\text{-}6,6')}$ = 3.1-4.2 ppm	$I_{H3\text{-}6,6'}$ = 3.00	Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN.
$\delta_{(H1)}$ = 4.588 ppm	I_{H1} = 0.35	One anomeric proton (1H) of the glucosamine units
$\delta_{(H1)}$ = 5.533 ppm	$I_{H1'}$ = 0.21	One anomeric proton (1H) of the N-acetyl glucosamine units

DS (%)= 38.07, 37.18, Average **DS** = **37.6 %**

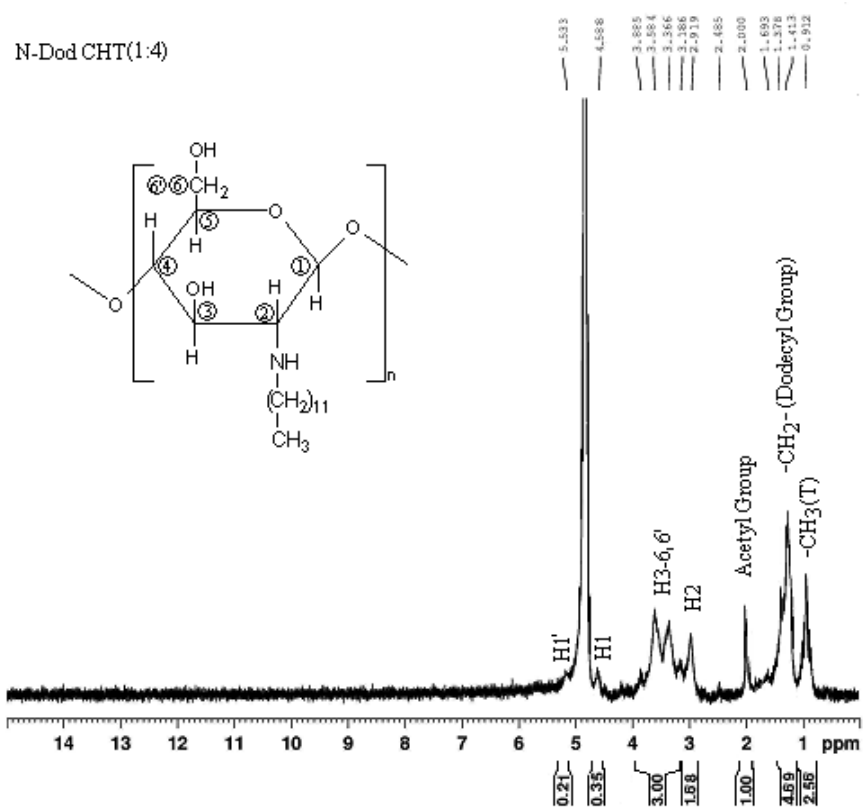


Figure 4.13 [1]HNMR spectrum of *N*- dodecyl chitosan (1:4)

[1]NMR spectrum analysis of N- dodecyl N, N-dimethyl chitosan chloride (1:4) [N-DodQCHT(1:4)]

The [1]HNMR spectrum of *N*- dodecyl N, N-dimethyl chitosan chloride (1:4) is shown in Figure 4.14.

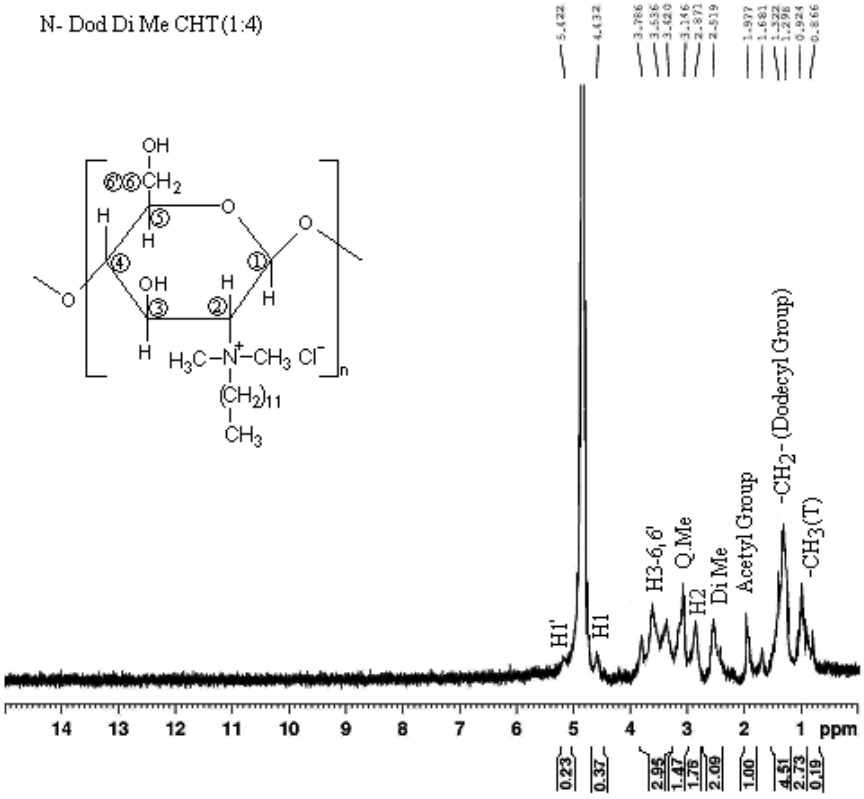


Figure 4.14 [1]HNMR spectrum of *N*- dodecyl *N, N*-dimethyl chitosan chloride (1:4)

Various peaks (δ) with corresponding integrals (I) for N-Dod Q CHT(1:4) depicted by [1]HNMR and the DQ determined using equation 4.12 are summarized as below.

$\delta_{Me(t)}$= 0.924ppm	$I_{Me(T)}$ =2.73	Three protons (3H) of terminal methyl of dodecyl chain.
$\delta_{(CH2)}$ =1.298ppm	I_{Dod} = $I_{(CH2)11-}$ = 4.51	22 protons (22H) of three methylene group of dodecyl chain
n = 25		25 protons dodecyl group,- ($CH_2)_{11}$-CH_3

$\delta_{(NAc)}$ =1.977ppm	I_{NAc} = 1.0	Three protons (3H) methyl terminal of acetyl group. -N-CO-C**H$_3$**
$\delta_{(H2)}$ = 2.871 ppm	I_{H2} = 1.76	One proton (1H) bound to C2 glucosamine (GlcN) residue.
$\delta_{(H3\text{-}6,6')}$ = 3.2-4.2 ppm	$I_{H3\text{-}6,6'}$ = 2.95	Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN.
$\delta_{(QMe)}$ =3.146ppm	I_{QMe}= 1.47	Six protons (6H) of two methyl groups attached to *N*- dodecyl substituted of GlcN residue.
$\delta_{(DiMe)}$=2.519ppm	I_{DiMe}= 2.09	Six protons (6H) of two methyl groups attached to free amino groups of GlcN residue.
$\delta_{(H1)}$ = 4.432 ppm	I_{H1} = 0.37	One anomeric proton (1H) of the glucosamine units.
$\delta_{(H1')}$ = 5.422 ppm	$I_{H1'}$ = 0.23	One anomeric proton (1H) of the N-acetyl glucosamine units.
δ = 0.866 ppm	I= 0.19	

DS (%) =37.6 %, DQ (%) =40.8 %

4.3.1.2.4 Elemental analysis

The degree of substitution (DS) of *N*- substituted CHT was calculated from C/N value of elemental analysis using the formula 4.9 [18, 60].

$$\frac{C1}{N1} \times (1 - DS) + \frac{C2}{N2} \times DS = \frac{C3}{N3} DAC \qquad \textbf{(4.9)}$$

Where, C1/N1 is calculated from the formula of non substituted CHT i.e. glucosamine residue (GlcN), C2/N2 from the N-Substituted residue and C3/N3 is found value of sample by elemental analysis. DAC is degree of deacetylation, 0.9 (i.e.90 %.).The percentage CHN content of selected chitosan derivatives determined by the elemental analysis is presented in Table 4.13 and the evaluated DS values of these derivatives in Table 4.19.

Table 4.13 Elemental analysis (CHN) data of different *N*-sub CHT derivatives

Sample	Theoretical values		Elemental Analysis,			
	C1/N1	C2/N2	C, %	H , %	N, %	C3/N3
CHT	5.14	6.86	35.52	6.75	5.33	5.33
TMCHT (1:10)	5.14	7.71	40.19	7.04	6.26	6.26
TMCHT (1:15)	5.14	7.71	44.63	7.07	7.11	7.11
N-Et CHT (1:2)	5.14	6.86	40.84	7.24	6.62	6.62
N-Bu CHT(1:2)	5.14	8.57	44.97	7.84	7.36	7.36
N-Dod CHT(1:4)	5.14	15.43	59.06	8.33	10.20	10.20
N-Bz CHT (1:4)	5.14	11.14	50.58	7.53	8.53	8.53
N-Np CHT(1:4)	5.14	14.57	54.38	7.96	9.36	9.36

C1/N1 is calculated from the formula of non substituted CHT i.e. glucosamine (GlcN) residue, C2/N2 from the formula of N-Substituted residue using the Table 4.12

Calculations:

Determination of DS of N-ethyl chitosan (1:2) [N-Et CHT (1:2)]

The DS determined from the elemental (CHN) analysis data and using the expression 4.9 for N-Et CHT (1:2) can be illustrated as follows.

$$\frac{C1}{N1}\times(1-DS)+\frac{C2}{N2}\times DS=\frac{C3}{N3}DAC \qquad \textbf{(4.9)}$$

$$\frac{C1}{N1}\times(1-DS)+\frac{C2}{N2}\times DS=\frac{C3}{N3}\times 0.9$$

$$5.14\times(1-DS)+6.86\times DS=6.62\times 0.9$$

$\therefore$ DS = 0.4756 ethyl groups per glucosamine unit OR 47.6 %

Similarly, the DS of *N*-butyl chitosan (1:2)[N-BuCHT (1:2)] and *N*-dodecyl chitosan (1:4)[N-DodCHT (1:4)] was found to be 43.27 % and 39.26 % respectively

4.3.1.2.5 Conductometric titrations

Degree of quaternization of quaternized *N*-alkyl chitosan chloride derivatives were also determined conductometrically by the titration against 0.1M $AgNO_3$ and using the expression 4.1 as discussed earlier in section 4.3.1.1.3.

Table 4.14 Conductometric titrations readings for *N*-alkyl Q CHT derivatives

$AgNO_3$ (0.1M)	Conductance (mMhos)											
	N-Et Q CHT (1:2)			N-Et Q CHT (1:4)			N-Bu Q CHT (1:2)			N-Bu Q CHT (1:4)		
	I	II	III	I	II	III	I	II	III	I	II	III
0	3.30	3.30	3.40	3.70	3.75	3.70	4.00	4.00	4.00	4.10	4.10	4.00
0.5	3.25	3.20	3.25	3.65	3.70	3.70	3.75	3.80	3.90	4.00	4.00	3.90
1.0	3.15	3.10	3.20	3.50	3.50	3.55	3.65	3.75	3.75	3.75	3.80	3.80
1.5	2.95	3.00	3.00	3.30	3.40	3.40	3.50	3.60	3.65	3.55	3.60	3.75
2.0	2.80	2.85	2.80	3.20	3.30	3.35	3.30	3.40	3.35	3.35	3.35	3.35
2.5	2.70	2.75	2.65	3.05	3.25	3.25	3.15	3.25	3.25	3.20	3.25	3.30
3.0	2.50	2.60	2.60	2.95	3.00	2.95	3.00	3.15	3.10	3.00	3.00	3.15
3.5	2.45	2.50	2.50	2.85	2.90	2.90	2.95	3.10	3.10	2.75	2.80	2.80
4.0	2.35	2.30	2.35	2.60	2.70	2.75	2.60	2.75	2.65	2.65	2.75	2.70
4.5	2.15	2.20	2.25	2.40	2.60	2.60	2.50	2.70	2.60	2.50	2.50	2.60
5.0	2.18	2.15	2.15	2.30	2.50	2.35	2.30	2.50	2.55	2.25	2.30	2.30
5.5	2.00	2.05	2.10	2.25	2.35	2.30	2.25	2.40	2.35	2.00	2.10	2.15
6.0	1.80	1.85	1.85	2.15	2.20	2.15	2.00	2.05	2.10	1.90	2.00	2.10
6.5	1.75	1.80	1.85	1.95	2.00	2.00	1.75	1.80	1.90	1.75	1.75	1.75
7.0	1.60	1.65	1.60	1.85	1.90	1.90	1.60	1.65	1.75	1.70	1.70	1.70
7.5	1.5	1.6	1.5	1.75	1.80	1.85	1.50	1.50	1.55	1.75	1.75	1.75
8.0	1.35	1.40	1.40	1.55	1.70	1.65	1.60	1.60	1.50	2.00	2.00	2.05
8.5	1.25	1.30	1.35	1.50	1.55	1.60	1.35	1.35	1.35	-	-	-
9.0	1.20	1.25	1.25	1.40	1.50	1.50	1.75	1.75	1.80	2.90	2.95	2.95
9.5	1.10	1.15	1.15	1.35	1.40	1.45	-	-	-	-	-	
10.0	1.00	1.05	1.05	1.25	1.30	1.35	2.20	2.25	2.20	3.75	3.70	3.70
10.5	1.25	1.25	1.25	1.35	1.35	1.40	-	-	-	-	-	-
11.0	2.00	1.95	2.00	2.00	2.00	2.05	3.60	3.60	3.65	4.50	4.60	4.55
12.0	3.50	3.40	3.50	3.25	3.00	3.30	4.50	4.40	4.50	5.40	5.50	5.50
13.0	4.90	5.00	4.90	4.50	4.60	4.60	5.40	5.50	5.40	6.25	6.25	6.30
14.0	6.25	6.30	6.30	6.00	5.90	6.05	6.25	6.25	6.30	7.00	7.05	7.10
15.0	7.90	7.80	7.75	7.25	7.30	7.25	7.20	7.25	7.25	7.90	8.00	7.90

NMP=40ml, CHT:CH_3I=1:15, CHT: NaOH =1:2

Table 4.15 Conductometric titrations readings for *N*-alkyl Q CHT derivatives

$AgNO_3$ (0.1M)	Conductance (mMhos)					
	N-Dod Q CHT (1:2)			N-Dod Q CHT (1:4)		
	I	II	III	I	II	III
0	3.70	3.65	3.75	3.80	3.75	3.80
0.5	3.50	3.45	3.60	3.65	3.60	3.70
1.0	3.40	3.30	3.50	3.50	3.65	3.60
1.5	3.15	3.10	3.15	3.30	3.25	3.35
2.0	3.00	2.90	3.00	3.25	3.20	3.30
2.5	2.75	2.70	2.80	3.00	3.00	3.00
3.0	2.60	2.55	2.70	2.85	2.85	2.90
3.5	2.40	2.45	2.55	2.75	2.65	2.70
4.0	2.25	2.25	2.30	2.55	2.50	2.60
4.5	2.15	2.20	2.20	2.40	2.45	2.50
5.0	2.15	2.15	2.20	2.35	2.35	2.35
5.5	2.25	2.25	2.25	2.20	2.25	2.25
6.0	2.60	2.60	2.60	2.25	2.20	2.25
6.5	-	-	-	2.50	2.50	2.50
7.0	3.25	3.20	3.25	3.60	3.60	3.65
8.0	3.90	3.85	3.80	4.25	4.30	4.30
9.0	4.50	4.50	4.50	5.00	5.00	5.00
10.0	5.00	5.00	5.10	5.75	5.80	5.80
11.0	5.65	5.70	5.70	6.50	6.55	6.50
12.0	6.25	6.25	6.30	7.25	7.25	7.25
13.0	6.90	6.85	6.90	8.00	7.90	8.00
14.0	7.40	7.50	7.50	8.60	8.60	8.65

NMP=40ml, CHT:CH_3I=1:15, CHT: NaOH =1:2

The calculation part is discussed below.

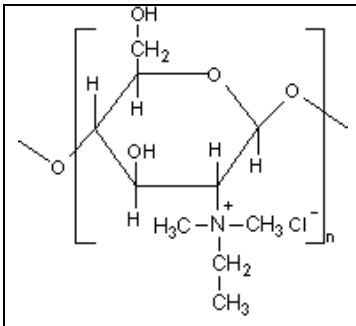
$$DQ\ (\%) = \frac{M_Q \times V \times [AgNO_3]}{m} X 100 \qquad \textbf{(4.1)}$$

Where,

M_Q is the molecular weight (g/mol) of repeating unit of the sample containing quaternized site, these values were obtained from the respective structural formula of derivatives given in Table 4.12. V and [$AgNO_3$] are the equivalent volume and concentration of $AgNO_3$ aqueous solution (0.1M) respectively and *m* (g) is the mass of

the sample which was 0.5g. The conductometric titration readings for *N*-alkyl Q CHT derivatives are presented in Table 4.14 and Table 4.15 and the calculated DQ values in Table 4.16 and Table 4.19.

DQ of N-ethyl N, N- dimethyl chitosan (1:2) chloride[N-Et Q CHT(1:2)]



C,10 X 12 =	120
O, 4 X 16 =	64
H, 20 X 1 =	20
N,1 X 14 =	14
Cl,1X 35.5 =	35.5
M_Q =	253.5

M_Q= 253.5, m= 0.5 g, V = 10.2, 10.2, 10.4 = 10.27 ml **or** V= 0.01027 L

$$\text{DQ (\%)} = \frac{M_Q \times V \times [AgNO_3]}{m} X100$$

$$\text{DQ (\%)} = \frac{253.5 \times 0.01027 \times 0.1}{0.5} X100 = \mathbf{52.0\ \%}$$

DQ of N-ethyl N,N-dimethyl chitosan (1:4) chloride[N-Et Q CHT(1:4)]

M_Q= 253.5, m= 0.5 g, V= 10.3, 10.2, 10.4 = 10.3 ml or V= 0.0103 L

$$\text{DQ (\%)} = \frac{M_Q \times V \times [AgNO_3]}{m} X100$$

$$\text{DQ (\%)} = \frac{253.5 \times 0.0103 \times 0.1}{0.5} X100 = \mathbf{52.2\ \%}$$

Similarly, the DQ of other derivatives determined are presented in Table 4.16

Table 4.16 Volume of 0.1M $AgNO_3$ required for lowest conductance value for different *N*-Alkyl Q CHT derivatives

Sample	0.1 M $AgNO_3$ titrant (V), ml				DQ, %
	I	II	III	Average	
N-Et Q CHT (1:2)	10.2	10.2	10.4	10.27	52.0
N-Et Q CHT (1:4)	10.3	10.2	10.4	10.30	52.2
N-Bu Q CHT (1:2)	8.4	8.4	8.5	8.43	47.5
N-Bu Q CHT (1:4)	7.3	7.3	7.2	7.27	40.9
N-Dod Q CHT (1:2)	5.9	5.8	6.0	5.90	46.4
N-Dod Q CHT (1:4)	5.7	5.8	5.7	5.73	45.1

NMP=40ml, CHT:CH_3I=1:15, CHT: NaOH =1:2

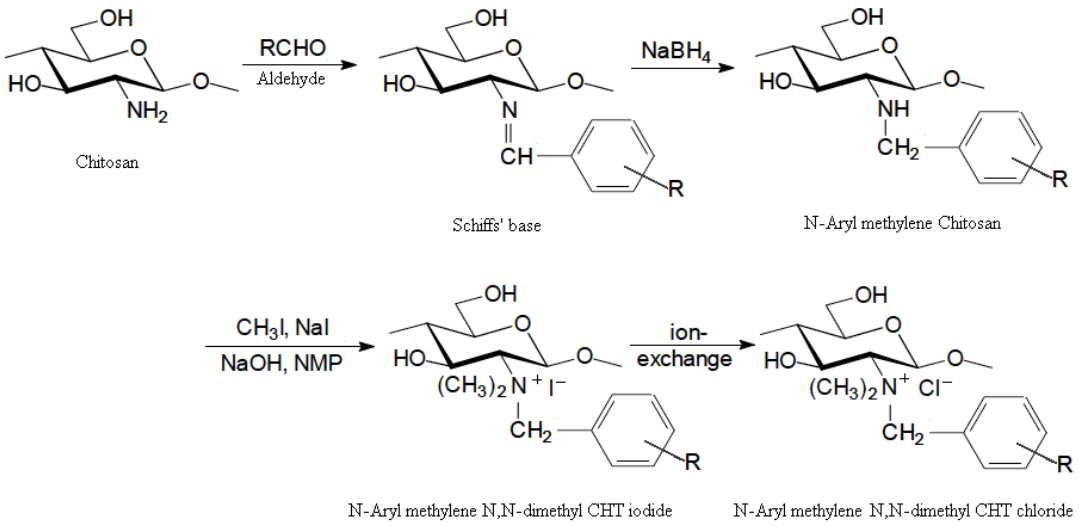
4.3.1.3 Synthesis of N-aryl N, N-dimethyl chitosan chloride

Analogous to aliphatic aldehyde, different aromatic aldehydes namely benzaldehyde and 1-naphthyl aldehyde were employed in the Bosch reduction methodology in this project. Same two step protocol i.e. first, the reaction of CHT with aromatic aldehyde in acidic medium to form Schiff's base followed by the second step of reduction of Schiff's base to form secondary amine was followed. These *N*-substituted CHT derivatives were then subjected to quaternization by reaction with methyl iodide (fifteen fold excess) as discussed previously. Possibility of external control on the degree of substitution was studied by varying the mole proportions of the aldehyde by two fold excess and four fold excess with respect to the amine of chitosan. Concentrations of various reaction ingredients i.e. aromatic aldehydes and sodium borohydride ($NaBH_4$) are mentioned in Table 4.11 and the nomenclature of synthesized *N*-aryl CHT and quaternized *N*- aryl CHT in Table 4.12.

4.3.1.3.1 Reaction mechanism

The reaction mechanism is similar to that of aliphatic aldehyde. In brief, the primary amines of CHT readily add to the carbonyl group (>C=O) of aldehydes to form α- hydroxy amines, also called carbinolamines. These species undergo spontaneous elimination of water molecule to yield imines or Schiff's base [22]. This is also an electrophilic substitution reaction and follows S_N2 mechanism. The carbon-oxygen bond in carbonyl group of aldehydes is highly polarized due to the presence of electro-ve

oxygen. The electrons constituting the π bonds are partially shifted towards oxygen as a result of electromeric effect. It implies that the carbon atom of carbonyl group is electron deficient i.e. electrophile and therefore readily attacks nucleophilic amino group of CHT. The reaction schemes for the syntheses of *N*-benzyl *N,N* dimethyl chitosan chloride (N-Bz QCHT) and *N*-(1-naphthyl) methylene chitosan chloride (N-Np Q CHT) are illustrated in scheme 4.12.



Scheme 4.12 Synthesis *N*-aryl *N,N*-dimethyl chitosan chloride

4.3.1.3.2 FTIR analysis of N-aryl CHT derivatives

The FTIR spectra of *N*-benzyl and *N*-(1-Naphthyl) methylene chitosan and their corresponding quaternized derivatives are shown in Figure 4.15 and Figure 4.16 respectively. A strong absorption peak at around wave number 3081 cm-1 is assigned to C-H stretching of aromatic group and the band at 1456 cm-1 is one of the typical bands for C=C ring stretching of benzene. The aliphatic C-H stretch at about 2931 cm-1 is assigned to methylene group. In addition to aromatic C-H stretch and C=C ring stretch, a compound can be considered aromatic only if the spectrum has at least one strong absorption below 900 cm^{-1} due to C-H bend out of benzene plane (-C=C-H bend) which are positioned at 896, 744 and 698 cm^{-1} in Figure 4.15 [66]. The increase in intensity in absorption peak at 1451 cm^{-1} in arylated quaternized chitosan in N-Bz Di Me CHT spectrum characterizes the attachment of methyl group.

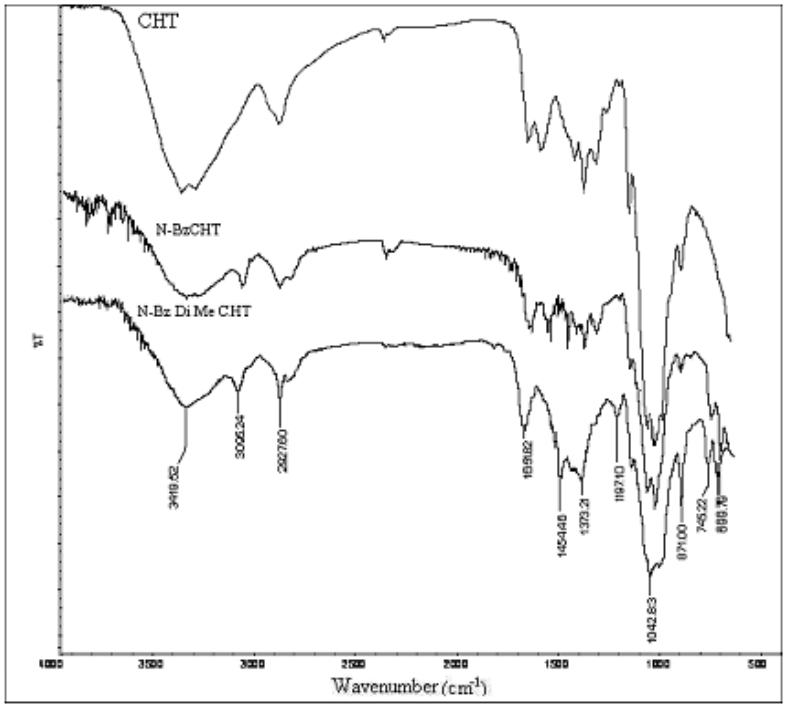


Figure 4.15 FTIR spectra of *N*-benzyl *N*,*N*-dimethyl chitosan chloride

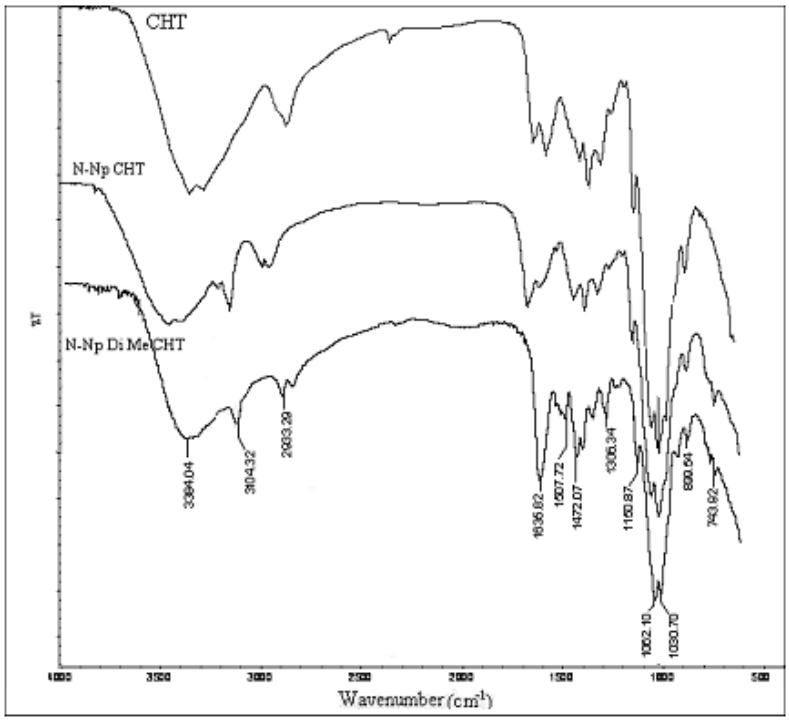


Figure 4.16 FTIR spectra of *N*-(1-naphthyl) methylene *N*,*N*- dimethyl chitosan chloride derivative

Similar patterns are observed in *N*-(1-Naphthyl) methylene chitosan, Figure 4.16. These spectra of aryl substituted chitosan derivatives characterize successful attachment of benzyl and 1-naphthyl methylene groups and the also the methyl groups at nitrogen atom of CHT amine.

4.3.1.3.3 ^{1}HNMR spectroscopy

In the ^{1}HNMR spectrum, the aromatic proton resonances appear in the downfield region, mostly in δ =6 to 7 ppm, compared to the residual sugar protons and therefore they can be integrated with minimal interference leading to greater accuracy. Comparing the integrals due to aromatic protons with that of proton bonded to C2 or protons bonded to the sum of C2 and C3-6, 6'; one can evaluate the degree of substitution using the equations 4.11 and 4.13. The degree of substitution and degree of quaternization of these N-Aryl CHT determined from ^{1}HNMR spectroscopy are presented in Table 4.19. The interpretations ^{1}HNMR spectra of N- Bz CHT and N-Np CHT and their quaternized derivatives are discussed below.

^{1}NMR Spectrum analysis of N- benzyl chitosan (1:4) [N- Bz CHT (1:4)]

The ^{1}HNMR spectrum of the *N*-benzyl Chitosan is shown in Figure 4.17.

The detailed analysis may be summarized as follows:

δ_{Ar}= 6.693 ppm	I_{Ar} = 2.41	Five protons (**5H**) of aromatic group.
n = 5		Aromatic protons.
$\delta_{(NAc)}$ =1.983 ppm	I_{NAc} = 1.0	Three protons (3H) methyl terminal of acetyl group, -N-CO-C**H$_3$**
$\delta_{(H2)}$ = 2.952 ppm	I_{H2} = 1.05	One proton (1H) bound to C2 glucosamine (GlcN) residue.
$\delta_{(H3\text{-}6,6')}$ = 3.2-4.5 ppm	$I_{H3\text{-}6,6'}$ = 5.54	Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN.
$\delta_{(H1)}$ = 4.692 ppm	I_{H1} = 0.53	One anomeric proton (1H)of the glucosamine units

$\delta_{(H1)}$ = 5.342 ppm $I_{H1'}$ = 0.34 One anomeric proton (1H) of the N-acetyl glucosamine units

DS (%) = 45.90 & 43.88, **Average DS = 45 %**

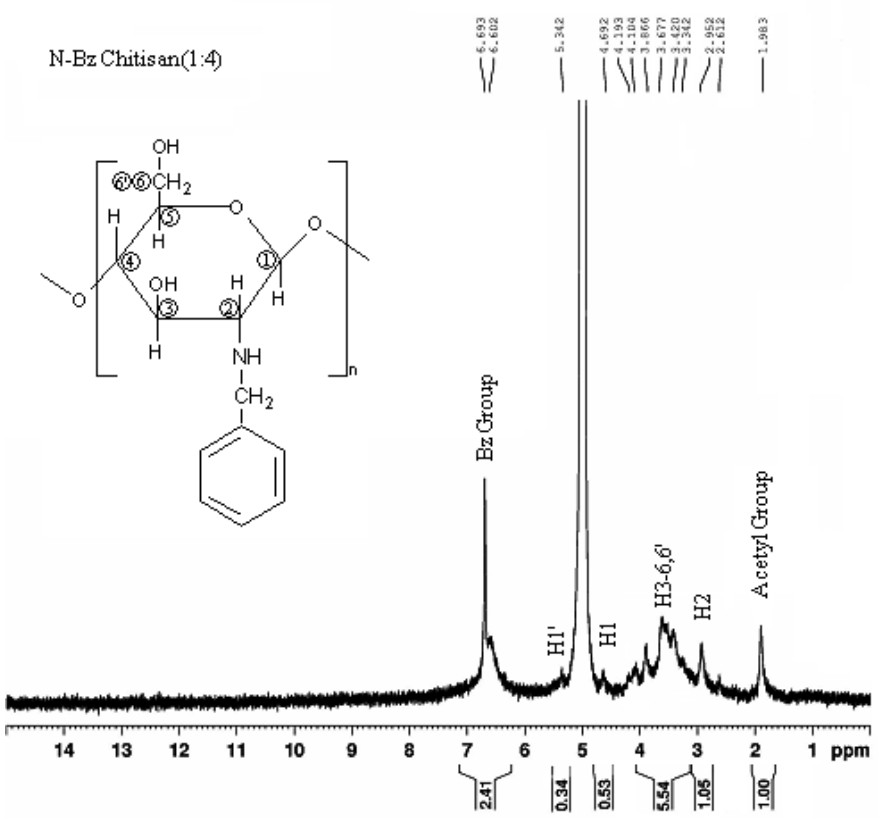


Figure 4.17 H^1NMR spectrum of N-Benzyl chitosan (1:4)

Calculations:

The degree of substitution can be determined using the equation 4.11 as follows:

$$\frac{A}{[B+C]} = \frac{nDS}{6} \quad \textbf{OR} \quad \frac{I_{Ar}}{[I_{H2} + I_{H3-6}]} = \frac{nDS}{6} \qquad \textbf{(4.11)}$$

The digit '6' at the denominator of right hand side is the total number of protons at C2 of GlcN and C3,4,5,6 & 6'.

Where, DS is the degree substitution per GLcN residue.

A = Peak area of substituent, A= I_{Ar} i.e. A= I_{Ar} = 2.41

B = Peak area of H2 (proton at C2) of glucosamine residue (GlcN).

i.e. B = I_{H2} = 1.05 at $\delta_{(H2)}$ = 2.952ppm for proton at C2 of GlcN.

C = Peak area of protons bounded to C-3,4,5,6 & 6' of GlcN.

C = $I_{H3\text{-}6,6'}$ = 5.54 (at δ= 3.2 to 4.5)

n= Number of proton per substituent = 5

Substituting these values in equation 4.11,

$$\frac{5\times DS}{6} = \frac{2.41}{[1.05+5.54]} = \frac{2.41}{6.59}$$

DS (%) = **43.9 %**

In another method, the degree of substitution can be calculated using the equation 4.13,

$$\frac{\textit{Signal Intensity due to H2}}{\textit{Signal Intensity due to aromatic protons}} = \frac{\textit{No of C2 protons per GlcN residue}}{\textit{No of aromatic protons per GlcN residue}}$$

$$\frac{I_{H2}}{I_{Ar}} = \frac{\textit{No of C2 protons per GlcN residue}}{\textit{No of aromatic protons per GlcN residue}} \qquad \textbf{(4.13)}$$

Number of protons bonded to C2 of GlcN residue is 1.

Let DS is the degree of substitution in % and 'n' is the number of protons bound to aromatic carbons.

Therefore, no of aromatic protons/ GlcN residue = $\frac{n\times DS}{100} = \frac{5\times DS}{100}$

$$\frac{I_{H2}}{I_{Ar}} = \frac{1}{\frac{5\times DS}{100}} \text{ OR } \frac{1\times 100}{5\times DS}$$

$$\text{DS} = \frac{1\times I_{Ar}\times 100}{5\times I_{H2}} = \frac{2.41\times 100}{5\times 1.05} = \textbf{45.9 \%}$$

Average DS = 45 %

[1]NMR Spectrum Analysis of N- benzyl N, N dimethyl chitosan chloride (1:4) [N-Bz Q CHT(1:4)]

The [1]HNMR spectrum of the *N*-benzyl *N,N* dimethyl chitosan chloride (1:4) is shown in Figure 4.18. In [1]HNMR spectrum**,** the signal δ_{Ar}= 6.602 ppm having the integral I_{Ar} = 2.24 is assigned to benzyl group. The signals due to protons of quaternary methyl groups (two methyl groups attached to benzyl substituted N of GlcN residue) was found at δ_{QMe} = 3.261ppm with the intensity I_{QMe} = 1.63.Methylation on unsubstituted amino groups was also traced at $\delta_{(DiMe)}$ =2.512 with the integral I_{DiMe}= 1.71. Other important signals recognized were: δ_{NAc} =1.961 ppm with integral I_{NAc} = 1.0 for acetyl group, δ_{H2} = 2.897 ppm; I_{H2} = 1.01 for proton bonded to C2 of GlcN residue, $\delta_{H3\text{-}6,6'}$ = 3.3-4.5 ppm; $I_{H3\text{-}6,6'}$ = 4.61 and the anomeric protons at $\delta_{(H1)}$ = 4.695 ppm; I_{H1} = 0.47 and $\delta_{(H1)}$ = 5.304 ppm; $I_{H1'}$ = 0.33.The average DS determined earlier for the sample before quaternization was 43.88 % and the DQ % calculated from the equation 4.12 was 33.96 %.

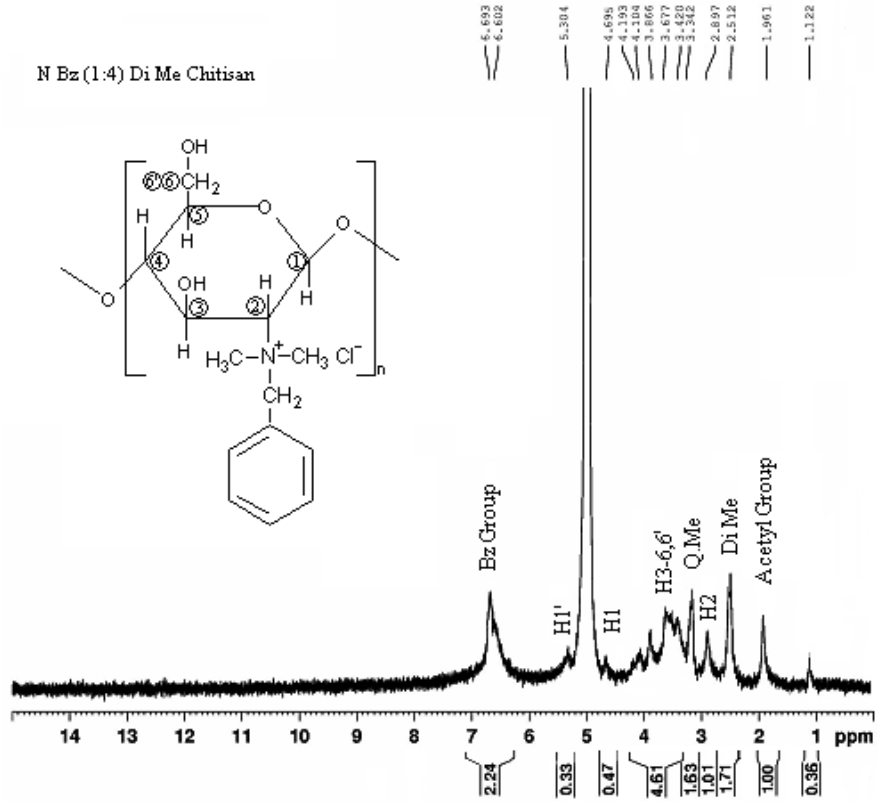


Figure 4.18 [1]HNMR spectrum of *N*- benzyl *N, N*- dimethyl chitosan chloride(1:4)

Calculations:

The degree of quaternization (DQ %) can be calculated using the equation 4.12 illustrated as follows.

$$DQ = \frac{I_{QMe}}{6\left[I_{H1} + I_{H1'}\right]} X100$$

$$= \frac{1.63}{6\left[0.47 + 0.33\right]} X100$$

= **34 %**

[1]NMR Spectrum analysis of N- Benzyl chitosan (1:2) [N- Bz CHT (1:2)]

Various peaks (δ) with corresponding integrals (I) for N-Bz CHT (1:4) depicted by ^{1}HNMR spectrum (figure not shown) and the DS determined using expressions 4.11 and 4.13 are summarized below.

δ_{Ar}= 6.7003ppm	I_{Ar} = 1.04	Five protons (**5H**) of aromatic group.
n = 5		Aromatic protons.
$\delta_{(NAc)}$ =1.986 ppm	I_{NAc} = 1.0	Three protons (3H) methyl terminal of acetyl group, -N-CO-C**H$_3$**
$\delta_{(H2)}$ = 3.001 ppm	I_{H2} = 1.18	One proton (1H) bound to C2 glucosamine (GlcN) residue.
$\delta_{(H3\text{-}6,6')}$ = 3.2-4.5 ppm	$I_{H3\text{-}6,6'}$ = 6.00	Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN.
$\delta_{(H1)}$ = 4.694 ppm	I_{H1} = 0.52	One anomeric proton(1H) of the glucosamine units
$\delta_{(H1')}$ = 5.341 ppm	$I_{H1'}$ = 0.38	One anomeric proton(1H) of the N-acetyl glucosamine units

DS= 17.63 % & 17.39 %, Average **DS =17.5 %**

[1]NMR Spectrum analysis of N-(1-naphthyl) methylene chitosan (1:4) [N- NpCHT (1:4)]

The ^{1}HNMR spectrum of the *N*-(1-naphthyl) methylene chitosan (1:4) [N-NpCHT (1:4) is shown Figure 4.19.

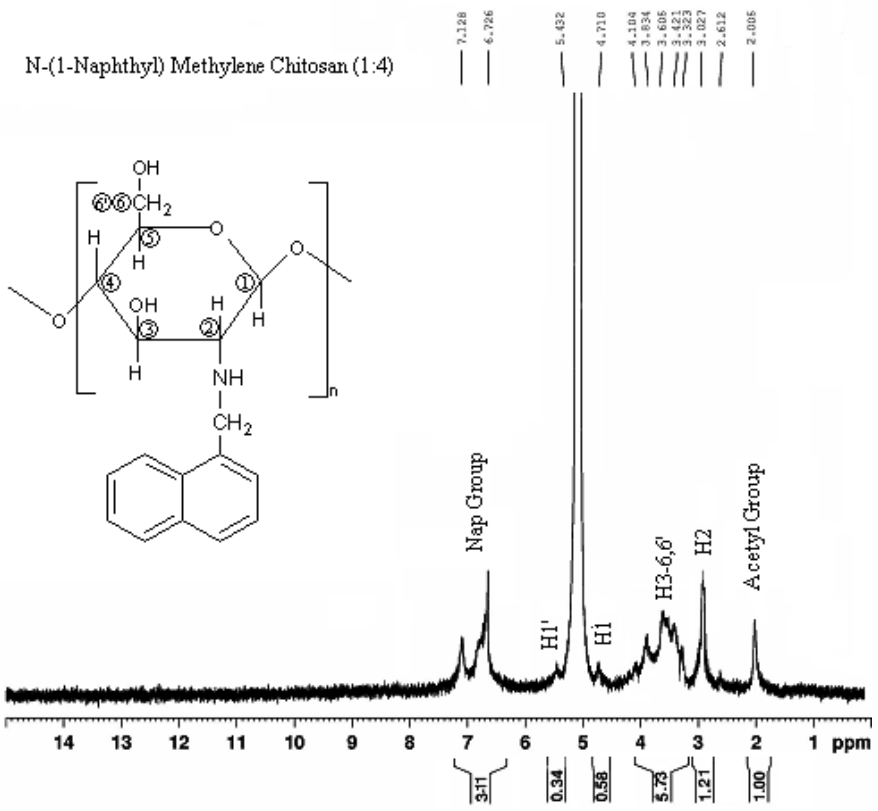


Figure 4.19 H[1]NMR spectrum of *N*-(1- naphthyl) methylene chitosan (1:4)

Various peaks (δ) with corresponding integrals (I) for N-Bz CHT (1:4) depicted by [1]HNMR spectrum and the DS determined using equations 4.11 and 4.13 are summarized as below.

δ_{Ar}= 6.726ppm	I_{Ar} = 3.11	Seven protons (**7H**) of aromatic group.
n = 7		Aromatic protons.
$\delta_{(NAc)}$ =2.006 ppm	I_{NAc} = 1.0	Three protons (3H) methyl terminal of acetyl group, -N-CO-C**H$_3$**
$\delta_{(H2)}$ = 3.027 ppm	I_{H2} = 1.21	One proton (1H) bound to C2 glucosamine (GlcN) residue.
$\delta_{(H3\text{-}6,6')}$ = 3.2-4.5 ppm	$I_{H3\text{-}6,6'}$ = 5.73	Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN.
$\delta_{(H1)}$ = 4.710 ppm	I_{H1} = 0.58	One anomeric proton (1H)of the glucosamine units

$\delta_{(H1')}$ = 5.432 ppm	$I_{H1'}$ = 0.47	One anomeric proton (1H) of the N-acetyl glucosamine units

DS= 36.72 & 38.41, Average **DS = 37.6 %**

[1]NMR spectrum analysis of N-(1- naphthyl) methylene N, N-dimethyl chitosan chloride (1:4) [N-Np Q CHT(1:4)]

The [1]HNMR spectrum of *N*-(1- naphthyl) methylene *N*, *N* dimethyl chitosan chloride (1:4) is shown in Figure 4.20.

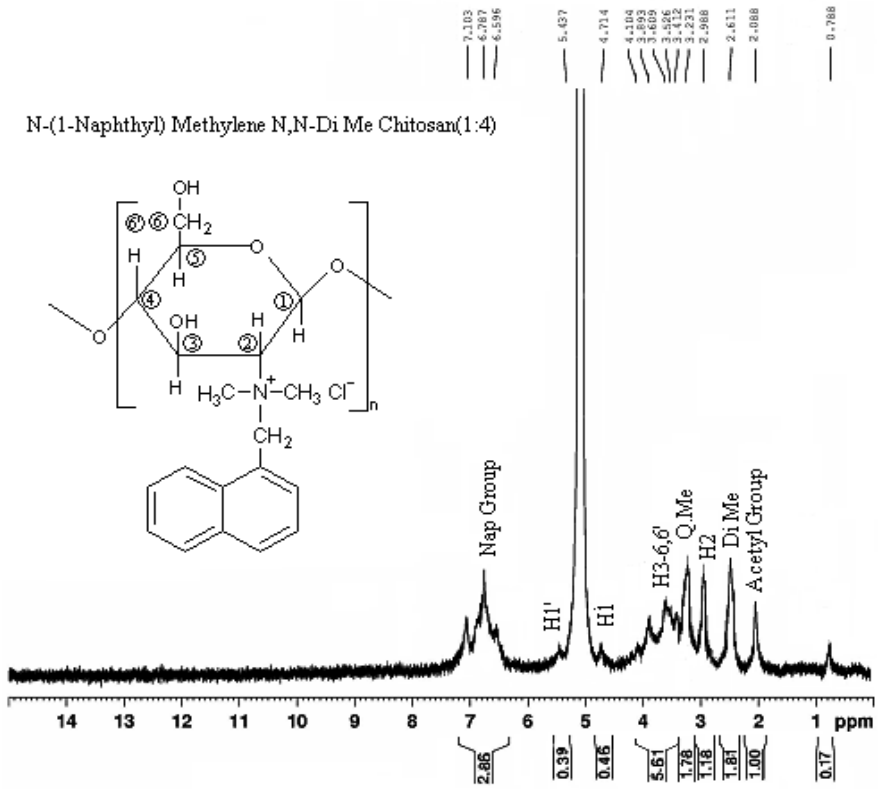


Figure 4.20 [1]HNMR spectrum of *N*-(1- naphthyl) methylene *N*, *N* dimethyl chitosan chloride (1:4)

Various peaks (δ) with corresponding integrals (I) for N-Np Q CHT (1:4) depicted by [1]HNMR and the DQ % calculated from the expression 4.12 are summarized as below.

δ_{Ar}= 6.596-	I_{Ar} = 2.86	Seven protons (7H) of aromatic group.

7.103 ppm		
n = 7		Aromatic protons.
δ_{NAc} =2.088 ppm	I_{NAc} = 1.0	Three protons (3H) methyl terminal of acetyl group, -N-CO-C**H_3**
δ_{H2} = 2.988 ppm	I_{H2} = 1.18	One proton (1H) bound to C2 glucosamine (GlcN) residue.
$\delta_{H3\text{-}6,6'}$ = 3.3-4.5	$I_{H3\text{-}6,6'}$ = 5.61	Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN.
δ_{QMe} = 3.231	I_{QMe} = 1.78	Six protons (6H) of two methyl groups attached to N-dodecyl substituted of GlcN residue.
$\delta_{(DiMe)}$ =2.611	I_{DiMe}= 1.81	Six protons (6H) of two methyl groups attached to free amino groups of GlcN residue.
$\delta_{(H1')}$ = 4.714	I_{H1} = 0.46	One anomeric proton (1H)of the glucosamine units
$\delta_{(H1)}$ = 5.437	$I_{H1'}$ = 0.39	One anomeric proton (1H) of the N-acetyl glucosamine units
DS =**37.6 %, DQ = 34.9 %**		

4.3.1.3.4 Elemental analysis

The degree of substitution (DS) of N- Benzyl CHT (1:4) and N-(1- Naphthyl) Methylene CHT was determined from C/N value of elemental analysis using the formula 4.9.

$$\frac{C1}{N1}\times(1-DS)+\frac{C2}{N2}\times DS=\frac{C3}{N3}DAC \qquad \textbf{(4.9)}$$

Where, C1/N1 is calculated from the formula of non substituted CHT i.e. glucosamine residue (GlcN), C2/N2 from the N-Substituted residue and C3/N3 is found value of sample by elemental analysis. DAC is degree of deacetylation, 0.9 (i.e.90 %.).The percentage CHN content of selected chitosan derivatives determined by the elemental analysis is presented in Table 4.13 and the evaluated DS values of these derivatives in Table 4.19. The calculations are illustrated as follows.

Calculations:

N- Benzyl chitosan (1:4) [N-Bz CHT (1:4)]

$$\frac{C1}{N1}\times(1-DS)+\frac{C2}{N2}\times DS=\frac{C3}{N3}DAC$$

$$5.14\times(1-DS)+11.14\times DS=8.53\times 0.9$$

DS = 0.4228 unit/GlcN residue OR **42.3 %**

N-(1-Naphthyl) methylene Chitosan (1:4) [N-NpCHT(1:4])

$$\frac{C1}{N1}\times(1-DS)+\frac{C2}{N2}\times DS=\frac{C3}{N3}DAC$$

$$5.14\times(1-DS)+14.57\times DS=9.36\times 0.9$$

DS = 0.3483 unit/GlcN residue OR **34.8 %**

4.3.1.3.5 Conductometric titrations

Degree of quaternization of quaternized N-alkyl chitosan chloride derivatives were also determined conductometrically by the titration against 0.1M $AgNO_3$ using the expression 4.1 as discussed earlier in section 4.3.1.1.3.

$$\text{DQ (\%)} = \frac{M_Q\times V\times[AgNO_3]}{m}X100 \qquad \textbf{(4.1)}$$

Where,

M_Q is the molecular weight of repeating unit of the sample containing quaternized site, these values were obtained from the respective structural formula of derivatives given in Table 4.12. V and [$AgNO_3$] are the equivalent volume in litre and concentration of $AgNO_3$ aqueous solution (0.1M) respectively and *m* (g) is the mass of the sample which was 0.5g. The conductometric titration data for *N*-Bz Q CHT(1:2), *N*-Bz Q CHT (1:4) and *N*-Np Q CHT (1:4) are presented in Table 4.17 and the evaluated DQ values for the derivatives in Table 4.18 and Table 4.19.

Table 4.17 Conductometric titrations for *N*-aryl Q CHT derivatives

$AgNO_3$ (0.1M)	Conductance, mMhos								
	N-Bz Q CHT (1:2)			N-Bz Q CHT (1:4)			N-Np Q CHT (1:4)		
	I	II	III	I	II	III	I	II	III
0	3.90	3.90	3.90	4.00	4.00	3.90	3.70	3.70	3.75
0.5	3.75	3.80	3.85	3.90	3.90	3.80	3.50	3.60	3.65
1.0	3.55	3.55	3.60	3.75	3.70	3.75	3.25	3.45	3.40
1.5	3.35	3.35	3.40	3.50	3.50	3.70	3.30	3.25	3.25
2.0	3.25	3.25	3.30	3.35	3.40	3.50	2.80	2.80	3.00
2.5	3.00	3.00	3.10	3.25	3.20	3.25	2.60	2.85	2.90
3.0	2.80	2.90	2.90	3.10	3.15	3.10	2.50	2.75	2.75
3.5	2.75	2.75	2.85	3.00	3.00	2.90	2.25	2.50	2.45
4.0	2.65	2.70	2.70	2.80	2.75	2.80	2.00	2.25	2.25
4.5	2.40	2.50	2.40	2.75	2.70	2.80	1.80	2.00	1.90
5.0	2.25	2.25	2.30	2.50	2.50	2.55	1.75	1.90	1.90
5.5	2.25	2.25	2.25	2.50	2.40	2.45	1.70	1.85	1.85
6.0	2.10	2.10	2.15	2.35	2.40	2.35	2.00	2.00	2.10
6.5	1.90	2.00	2.00	2.25	2.30	2.25	-	-	-
7.0	2.25	2.20	2.25	2.15	2.30	2.35	2.70	2.60	2.60
7.5	2.50	2.55	2.50	2.75	2.70	2.75	-	-	-
8.0	2.85	2.85	2.85	3.00	3.00	3.00	3.50	3.85	3.85
9.0	3.50	3.50	3.50	3.80	3.85	3.75	4.25	4.15	4.10
10.0	4.25	4.25	4.25	4.50	4.60	4.60	4.90	5.00	5.00
11.0	5.00	5.00	4.90	5.40	5.40	5.35	5.00	4.20	5.25
12.0	5.75	5.75	5.70	6.25	6.20	6.30	6.40	6.50	6.50
13.0	6.40	6.40	6.35	6.90	6.90	7.00	7.25	7.25	7.25
14.0	7.15	7.20	7.25	7.70	7.75	7.75	7.80	7.90	8.00

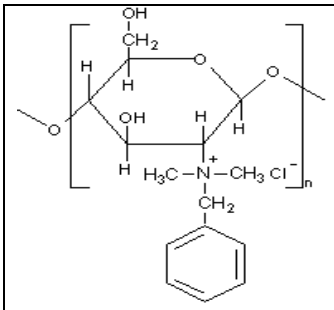
CHT: CH_3I (1:15), CHT: NaOH (1:2)

Table 4.18 Conductometric method for determination DQ of *N*-aryl Q CHT derivatives

Sample	0.1M $AgNO_3$ titrant (V), ml				DQ, %
	I	II	III	Average	
N-Bz Q CHT (1:2)	6.6	6.6	6.8	6.66	42.07
N-Bz Q CHT (1:4)	6.6	6.6	6.5	6.56	41.44
N-Np Q CHT (1:4)	5.4	6.6	6.4	6.47	39.96

CHT:CH_3I=1:15, CHT: NaOH =1:2

DQ of N-benzyl N, N dimethyl chitosan chloride (1:4) [Q-Bz CHT(1:4)]



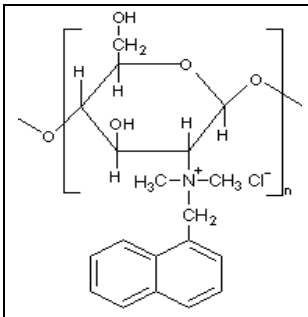
C,15 X 12 =	180
O, 4 X 16 =	64
H, 22 X 1 =	22
N,1 X 14 =	14
Cl,1X 35.5 =	35.5
M_Q =	315.5

M_Q = 315.5, m= 0.5 g, V = 6.6, 6.6, 6.5 = 6.57 ml or V= 0.00657 L

$$\text{DQ (\%)} = \frac{M_Q \times V \times [AgNO_3]}{m} X100$$

$$\text{DQ (\%)} = \frac{315.5 \times 0.00657 \times 0.1}{0.5} X100 = \mathbf{41.44\ \%}$$

N-(1-Naphthyl) methylene N, N-dimethyl chitosan chloride(1:4)[N-NpQCHT(1:4)]



C,19 X 12 =	228
O, 4 X 16 =	64
H, 24 X 1 =	24
N,1 X 14 =	14
Cl,1X 35.5=	35.5
M_Q =	365.5

M_Q = 365.5, m =0.5 g, V = 5.4, 6.6, 6.4 = 6.47 ml or V= 0.00647 L

$$\text{DQ (\%)} = \frac{M_Q \times V \times [AgNO_3]}{m} X100$$

$$= \frac{315.5 \times 0.00647 \times 0.1}{0.5} X100 = \mathbf{40\ \%}$$

Table 4.19 DS and DQ of *N*-substituted CHT

***N*- Alkyl/Aryl CHT**			***N*- Alkyl/Aryl Q CHT**		
Sample	**Degree of substitution (DS), %**		**Sample**	**Degree of quaternization (DQ), %**	
	H^1NMR analysis	**C/N analysis**		**H^1NMR analysis**	**Conductometry**
N-Et CHT (1:2)	45.5	47.6	N- Et Q CHT (1:2)	46.3	52.0
N-Et CHT (1:4)	82.6	-	N- Et Q CHT (1:4)	-	52.2
N-Bu CHT (1:2)	40.1	43.3	N- Bu Q CHT (1:2)	43.0	47.5
N-Bu CHT (1:4)	71.2	-	N- Bu Q CHT (1:4)	-	41.0
N-Dod CHT (1:2)	22.1	-	N- Dod Q CHT (1:2)	-	46.4
N-Dod CHT (1:4)	37.6	39.3	N-Dod Q CHT (1:4)	40.8	45.1
N-Bz CHT (1:2)	17.5	-	N-Bz Q CHT (1:2)	-	42.1
N-Bz CHT (1:4)	45.0	42.3	N-Bz Q CHT (1:4)	34.0	41.4
N-Np CHT(1:4)	37.6	34.8	N-Np Q CHT(1:4)	35.0	40.0

The value in parentheses indicate the CHT: CHO ratio,
The N- Alkyl/Aryl CHT were quaternized with CH_3I at fifteen fold excess

The DS and DQ determined using different analytical techniques for *N*-alkylated and *N*-arylated CHT and their quaternized derivatives are summarized in Table 4.19. It can be observed from the table that data obtained from different methods are quite nearer. The DQ determined by conductometry were found to be somewhat higher than that determined by ^{1}HNMR spectroscopy. This may be due to the presence of extra chloride ions associated with mono-, di- and trimethylated amino sites generated during quaternization reaction; and also to the presence of unbound chloride ions that was not completely removed during purification process of samples. Nevertheless, the conductometric titration methods are useful tool for the determination of DQ of quaternized samples since the same trend of ^{1}HNMR was followed. Further it was observed that the DS of *N*-aryl CHT derivatives determined by ^{1}HNMR method were higher than the results of elemental analysis. On the other hand, the trend was reversed in

case of *N*-alkyl CHT derivatives. In the spectrum of *N*-aryl derivatives, the aromatic proton resonances appear in the downfield region i.e. left to the D_2O signal, mostly in δ = 6 to 7 ppm, compared to the residual sugar protons and therefore they can be integrated with minimal interference. While, the signals due to protons bonded to *N*-alkyl groups appear together with signals of protons of saccharide i.e. in the region of δ <4.5 leading to many superimpositions. It is worthwhile to consider the ^{1}HNMR methodology as a more authentic for aryl derivatives.

It was also observed from the Table 4.19 that degree of alkylation for a given alkyl chain, as for example N-Et CHT, increased with concentration of aldehyde. However, at a given concentration of aldehyde the degree of substitution decreased with increase in chain length. Further, aromatic aldehydes were less effective substituent to form Schiff's base compared to the aliphatic aldehydes. In general, smaller size and aliphatic aldehydes are more effective substituents while bigger size and aromatic aldehydes give poor degree of substitution on chitosan. When these *N*-substituted CHT derivatives were further quaternized with methyl iodide, the degree of quaternization was also decreased with increase in molecular size of the alkyl/aryl substituents. As discussed earlier, the reaction of chitosan with aldehyde proceeds through electrophilic substitution reaction in which the carbonyl carbon of aldehyde, the electron deficient i.e. electrophile, reacts with nucleophilic amino group of chitosan. Thus for maximum reactivity towards nucleophiles, the carbonyl carbon should be as +ve as possible and not sterically hindered by adjacent groups. The alkyl groups attached to carbonyl carbon being electron releasing decreases the positivity of the carbon atom and also the bulky alkyl groups offer steric hindrance to the approaching amino group of chitosan. Thus, besides steric hindrance, with increase in alkyl chain length the reactivity of aldehyde is decreased and resulted into poor degree of substitution. In case of aromatic aldehydes the α-H is not involved in the reaction and the conjugation of carbonyl carbon with aryl ring reduces the electrophilic reactivity due to delocalized π-electrons. Hence aromatic aldehydes are less reactive than their aliphatic counterpart. This steric hindrance is also responsible for the decrease in quaternization with increase in molecular size of substituents.

4.3.2 Viscosity behavior of *N*- substituted CHT derivatives

Besides the estimation of molecular weight, the viscosity measurement data of polymer solutions are useful in studying the chain conformation. Various factors such as temperature, pH, electrolytes, molecular weight, polymer concentration, nature of counter ion etc are found to influence the conformational arrangements of poly electrolytes chains in aqueous solutions and also the viscosity [67]. Effect of quaternization of CHT and *N*-alkyl and *N*-aryl CHT derivatives on their viscosity behaviour and the intrinsic viscosity [η], a function of molecular weight, was evaluated. The solutions were prepared in acetic acid / sodium acetate solvent system with corresponding concentration of 0.25 M / 0.25 M recommended for the determination of molecular weight of chitosan using Mark-Houwink equation [68]. The average of three readings of flow time of various *N*-substituted Q CHT derivative solutions of different concentrations, in presence and absence of sodium acetate, are presented in Table 4.20 and Table 4.22 respectively. The reduced viscosities (η_{red}) [69] calculated from these readings using equations 2.7, 2.8 and 2.9(chapter 2) for polymeric solutions in presence and absence of sodium acetate are presented in Table 4.21 and Table 4.23 respectively and graphically in Figures 4.21, 4.22 and 4.23. The intrinsic viscosities obtained by extrapolation of these curves to intercept Y-axis of zero concentration are given in Table 4.24 and Figure 4.24.

Table 4.20 Viscometer readings of *N*- sub CHT solutions in presence of sodium acetate

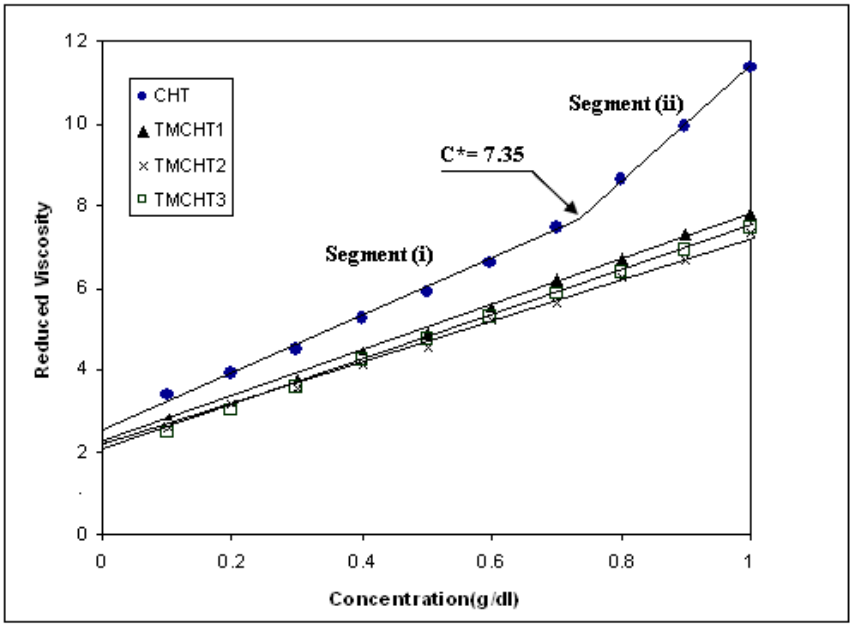
Conc, g/dl	Average flow time (T), seconds								
	CHT	**TMCHT 1**	**TMCHT 2**	**TMCHT 3**	**N-Et Q CHT (1:2)**	**N-Bu Q CHT (1:2)**	**N-Dod Q CHT (1:4)**	**N-Bz QCHT (1:4)**	**N-Np QCHT (1:4)**
0.1	21.27	20.28	19.98	19.74	19.76	20.16	20.41	20.20	20.03
0.2	28.27	26.22	25.96	25.33	25.96	26.34	27.11	26.66	26.79
0.3	37.23	33.72	32.87	32.87	33.44	34.15	35.87	36.44	36.01
0.4	49.14	43.80	42.21	42.53	43.36	44.94	47.80	46.09	47.67
0.5	62.61	54.59	51.89	53.48	54.91	56.81	60.70	59.91	59.04
0.6	78.69	68.24	65.09	65.96	72.05	68.24	76.24	70.91	75.10
0.7	98.32	84.75	78.52	80.97	84.19	88.63	96.30	91.41	92.52
0.8	125.28	100.81	95.22	96.62	100.93	108.93	115.15	111.47	113.76
0.9	157.41	120.28	111.57	114.28	119.42	127.42	140.13	131.28	143.13
1.0	196.00	139.66	132.52	133.94	142.04	150.77	162.19	156.00	163.46

Solvent: Acetic acid =0.25M, Sodium acetate = 0.25M, T_0= 15.87 sec, Temp 30 ^{0}C

Table 4.21 Reduced viscosity (η_{red}) of *N*-sub CHT solutions in presence of sodium acetate

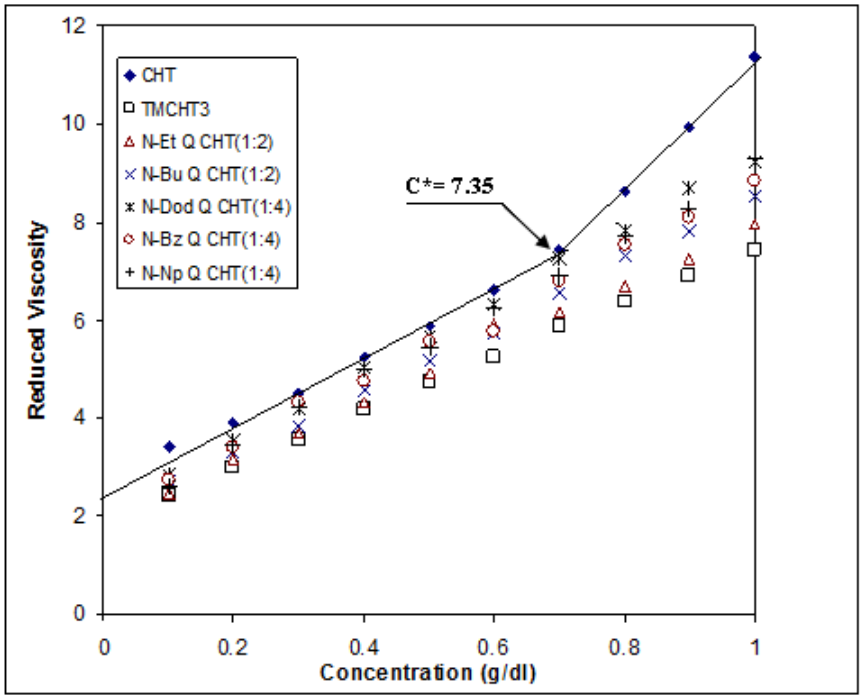
Conc, g/dL	Reduced Viscosity (η_{red})								
	CHT	TMCHT 1	TMCHT 2	TMCHT 3	N-Et Q CHT (1:2)	N-Bu Q CHT (1:2)	N-Dod Q CHT (1:4)	N-Bz QCHT (1:4)	N-Np QCHT (1:4)
0.1	3.40	2.78	2.59	2.44	2.45	2.70	2.86	2.73	2.62
0.2	3.91	3.26	3.18	2.98	3.18	3.30	3.54	3.40	3.44
0.3	4.49	3.75	3.57	3.57	3.69	3.84	4.20	4.32	4.23
0.4	5.24	4.40	4.15	4.20	4.33	4.58	5.03	4.76	5.01
0.5	5.89	4.88	4.54	4.74	4.92	5.16	5.65	5.55	5.44
0.6	6.60	5.50	5.17	5.26	5.90	5.74	6.34	5.78	6.22
0.7	7.42	6.20	5.64	5.86	6.15	6.55	7.24	6.80	6.90
0.8	8.62	6.69	6.25	6.36	6.70	7.33	7.82	7.53	7.71
0.9	9.91	7.31	6.70	6.89	7.25	7.81	8.70	8.08	8.28
1.0	11.35	7.80	7.35	7.44	7.95	8.50	9.22	8.83	9.30

Solvent: Acetic acid =0.25M, Sodium Acetate = 0.25M, T_0= 15.87 sec, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40



DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9

Figure 4.21 Reduced viscosity (η_{red}) TMCHT solutions in presence of sodium acetate



DQ (%):TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 45/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.22 Reduced viscosity (η_{red}) *N*- sub CHT solutions in presence of sodium acetate

Table 4.22 Viscometer readings of *N*- sub CHT solutions in absence of sodium acetate

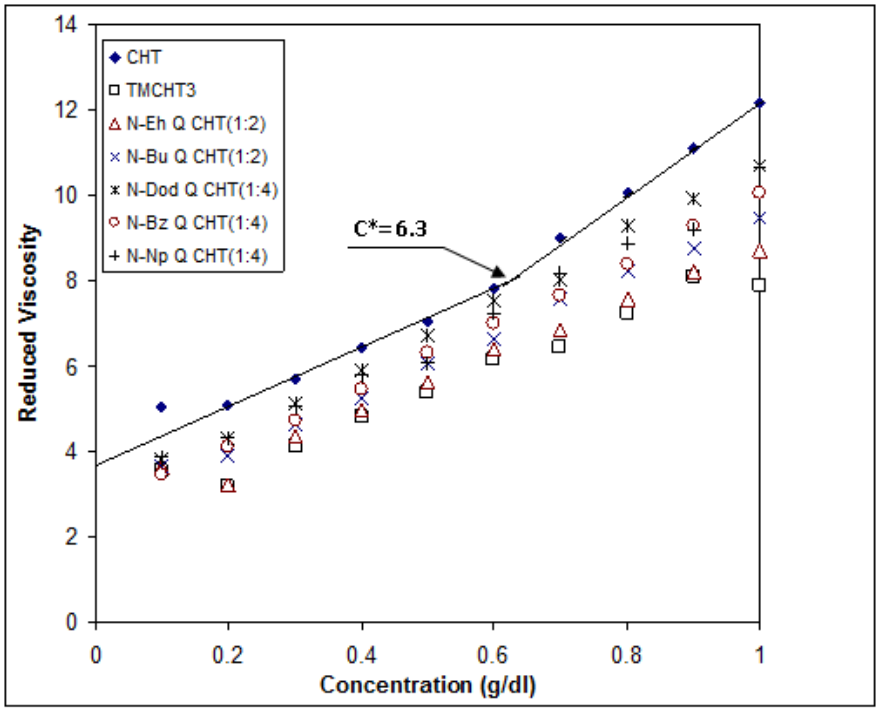
Conc, g/dL	Average flow time, sec						
	CHT	TMCHT3	N-Et QCHT (1:2)	N-Bu QCHT (1:2)	N-Dod QCHT (1:4)	N-Bz QCHT (1:4)	N-Np QCHT (1:4)
0.1	23.67	21.33	21.44	21.53	21.77	21.17	21.85
0.2	31.79	25.75	25.88	28.05	29.34	28.68	29.28
0.3	42.56	35.15	36.33	37.60	40.01	38.12	39.63
0.4	56.35	45.96	46.97	48.92	53.01	50.12	52.13
0.5	71.22	58.16	59.81	63.51	68.71	64.48	63.59
0.6	89.69	73.63	75.99	78.35	86.95	81.85	84.11
0.7	114.90	86.37	91.10	99.04	104.10	100.14	106.09
0.8	142.29	107.03	110.81	119.12	132.34	121.26	127.43
0.9	173.27	130.48	132.18	139.83	156.41	147.06	146.07
1.0	207.14	139.77	152.68	164.96	184.16	173.93	183.53

Solvent: Acetic acid =0.25M, T_0= 15.74 sec, DQ (%): TMCHT3= 50.9;
DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) =40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Table 4.23 Reduced viscosity (η_{red}) of *N*- sub CHT solutions in absence of sodium acetate

Conc, g/dL	Reduced Viscosity (η_{red})						
	CHT	TMCHT3	N-Et QCHT (1:2)	N-Bu QCHT (1:2)	N-Dod QCHT (1:4)	N-Bz QCHT (1:4)	N-Np QCHT (1:4)
0.1	5.04	3.55	3.62	3.68	3.83	3.45	3.88
0.2	5.10	3.18	3.22	3.91	4.32	4.11	4.30
0.3	5.68	4.11	4.36	4.63	5.14	4.74	5.06
0.4	6.45	4.80	4.96	5.27	5.92	5.46	5.78
0.5	7.05	5.39	5.60	6.07	6.73	6.32	6.08
0.6	7.83	6.13	6.38	6.63	7.54	7.00	7.24
0.7	9.00	6.41	6.84	7.56	8.02	7.66	8.20
0.8	10.05	7.25	7.55	8.21	9.26	8.38	8.87
0.9	11.12	8.10	8.22	8.76	9.93	9.27	9.20
1.0	12.16	7.88	8.70	9.48	10.70	10.05	10.66

Solvent: Acetic acid =0.25M, T_0= 15.74 sec, 30 ^{0}C, DQ (%):TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40



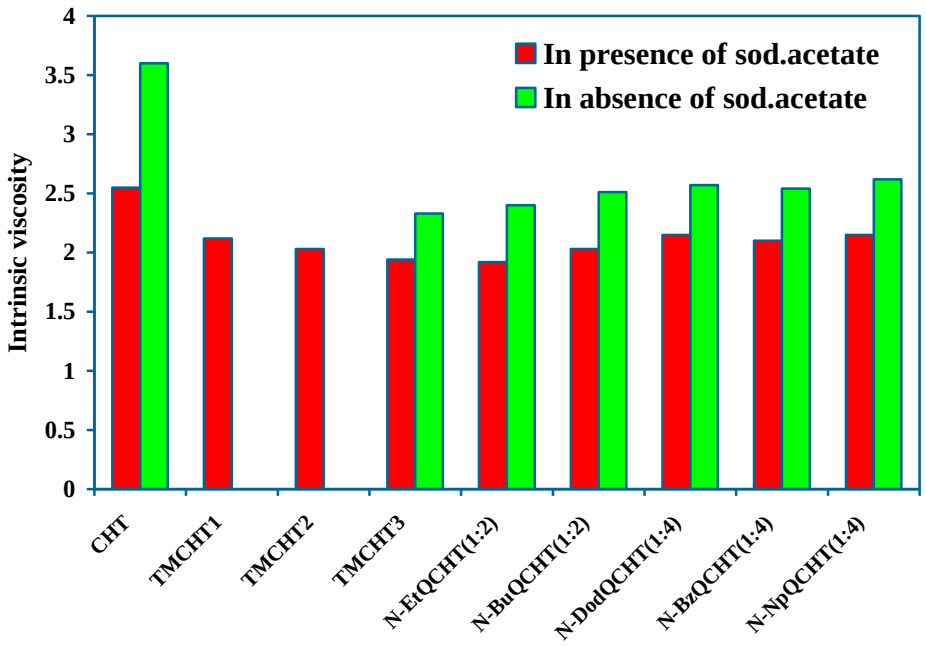
DQ (%):TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 45/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.23 Reduced viscosity (η_{red}) *N*- sub CHT solutions in absence of sodium acetate

Table 4.24 Effect of quaternization on intrinsic viscosity of CHT derivatives

Sample	In presence of Sodium Acetate		In absence of Sodium Acetate		Drop in [η] due to sodium acetate, %
	Intrinsic viscosity [η]	Slope	Intrinsic viscosity [η]	Slope	
CHT	2.55	*(i) 6.85 (ii)13.13	3.60	(i) 7.23 (ii) 12.42	29.1
TMCHT1	2.12	5.65	-	-	-
TMCHT2	2.03	5.23	-	-	-
TMCHT3	1.94	5.51	2.33	6.08	16.7
N Et Q CHT(1:2)	1.92	6.00	2.40	6.40	20.0
N Bu Q CHT(1:2)	2.03	6.48	2.51	6.99	19.1
N Dod Q CHT(1:4)	2.15	7.15	2.57	8.07	17.0
N Bz Q CHT(1:4)	2.10	6.37	2.54	7.30	17.3
N Np Q CHT(1:4)	2.15	6.87	2.62	7.71	17.9

** Segments of the curve i.e. Segment (i) and Segment (ii)DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 45/41.4, N-Np Q CHT(1:4)= 37.6/40*



DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.24 Effect of quaternization on intrinsic viscosity of CHT derivatives

The intrinsic viscosity, as observed from Table 4.24 and Figure 4.24, was dropped due to quaternization process indicating a depolymerization of parent chitosan. The drop in viscosity was substantial even at low concentrations of methyl iodide (i.e. at lower DQ) and was very slightly affected with further increase in methyl iodide concentration. This means the depolymerization of CHT occurred is not only attributed to the extent of quaternization but also to the reaction condition such as duration, temperature and the presence of ingredients i.e. sodium hydroxide and NMP. At almost similar levels of DS and DQ of *N*-substituted Q CHT derivatives, the intrinsic viscosity was found to be slightly increased with increase in chain length or molecular size of substituent. Presence of electrolyte i.e. sodium acetate in CHT derivative solutions reduced the intrinsic viscosity. The loss in viscosity was maximum of CHT solution and minimum of TMCHT3 solution. This apparent change in [η] due to electrolyte in solvent, however, does not mean the change in molecular weight of same sample in two different solvent systems, the Mark-Houwink constants α and K that actually change and not the molecular weight.

The curves for TMCHT in Figure 4.21 were found to be almost linear without any point of inflection or critical concentration (C*), apparently indicating scattered distribution of polymer molecules without aggregation. Such critical concentrations (C*) were observed in CHT solutions. When the curves for these polymer solutions were studied in absence of electrolyte (sodium acetate), Figure 4.23, some irregularities noticed. The position of C* for CHT solution was shifted left to 6.3 g/dL. TMCHT, here again, did not show any point of critical concentration but showed slight increased viscosity at high dilution/low concentration of paradoxical behaviour often observed in polyelectrolytes. The increased viscosity of poly cations at high dilutions may be attributed to the chain expansions due to electrostatic repulsion between same ions on macromolecule [58,66,70]. In presence of added electrolyte (sodium acetate), the charges will be screened and consequently the polyelectrolyte chain will adopt coiled conformation as demonstrated in Figure 4.25. Further these added electrolyte ions offer shielding effect to cause polymer molecules repel each other resulting into decreased viscosity [71]. Regardless the downward influence of depolymerization of CHT due to quaternization reaction and also due to the presence of electrolyte on viscosity, a

contradictory i.e. increase in viscosity of modified CHT is expected due to the introduction of bulkier side groups. The loss in molecular weight due to depolymerization during quaternization reaction is believed to overcome to some extent due to introduced side methyl groups that offer resistance to flow/slippages of molecules. It means the viscosity of TMCHT is governed by two opposite phenomena namely the fall in viscosity due to depolymerization during quaternization reaction and shielding effect of electrolytes; and the increase in viscosity due attached bulky methyl groups.

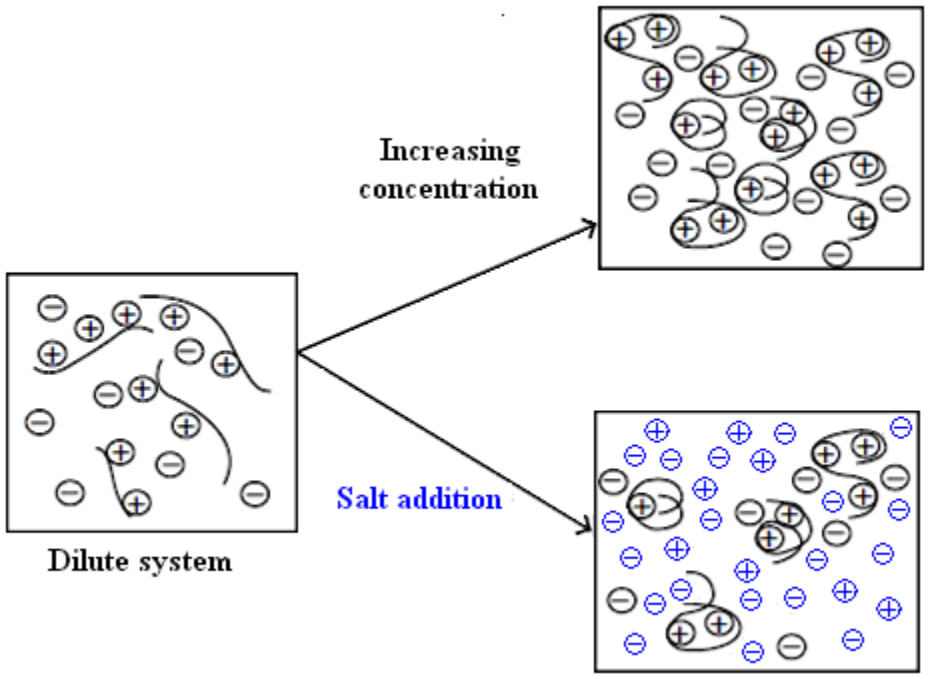


Figure 4.25 Polycations chain conformation as a function of polymer concentration and electrolyte

At about similar DS values of *N*- substituted Q CHT derivatives, the effect of molecular size of *N*-substituent on intrinsic viscosity was very much close to that of TMCHT derivatives nevertheless with some increased trend as shown in Table 4.24. It was observed from Figure 4.22 that the curves for all quaternized N-substituted CHT derivative solutions containing sodium acetate were almost linear without any inflections of critical concentrations (C*). The *N*- substituted Q CHT derivatives showed increased viscosities at higher concentrations as a function of chain length of substituent. The

resistance to flow or slippages of macromolecules may occur due to bulkier side groups and intra and inter molecular hydrophobic-hydrophobic interactions [72]. The possibility of contribution of aggregation of polyelectrolyte molecules at higher concentrations to viscosity is meager due to ionic repulsion but cannot be completely discarded. While comparing the influence of added electrolyte on chain conformation of *N*-substituted Q CHT derivatives, Figures 4.22, 4.23 and 4.24 envisage that the influence was maximum in CHT and lower CHT derivatives solutions where as it was nominal in solutions of higher substituted derivatives. In other words, the charge screening on quaternized sites was subdued due the chain length or molecular size of *N*-alkyl or *N*-aryl substituent.

4.3.3 Treatment of cotton fabric with *N*-substituted CHT derivatives

Chitosan and its *N*-substituted derivatives namely *N, N, N* -trimethyl chitosan chloride (TMCHT), *N*-alkyl chitosan and *N*-aryl chitosan and their quaternized derivatives, enumerated in Table 4.12, were applied on cotton fabric by conventional pad-dry-cure method. TMCHT of different DQ and *N*-alkyl/*N*-aryl CHT derivatives of almost similar DS and DQ respectively was selected for textile application. Concentrations of these derivatives for pad bath application are mentioned in Table 4.25.

Table 4.25 Application of *N*-sub CHT compounds on cotton fabric

***N*-Alkyl/Aryl CHT**		***N*- Alkyl/Aryl Q CHT**		**Conc in pad bath, g/L**		
Sample	**DS, %**	**Sample**	**DQ, %**			
Control	-	-	-	-	-	-
CHT	-	-	-	2.5	5	10
-	-	TMCHT1	13.4	2.5	5	10
-	-	TMCHT2	22.0	2.5	5	10
-	-	TMCHT3	50.9	2.5	5	10
N-Et CHT (1:2)	45.5	N-Et Q CHT (1:2)	51.7	2.5	5	10
N-Bu CHT (1:2)	40.1	N-Bu Q CHT (1:2)	47.5	2.5	5	10
N-Dod CHT(1:4)	37.6	N-Dod Q CHT (1:4)	45.1	2.5	5	10
N-Bz CHT (1:4)	45.0	N-Bz Q CHT (1:4)	41.4	2.5	5	10
N-Np CHT(1:4)	37.6	N-NpQ CHT (1:4)	40.0	2.5	5	10

Since the treated fabric samples were evaluated in many cases using optical instruments, any changes in fabric construction due to above treatments may lead to

variations in results. In order to minimize the error, a blank treatment to the fabric was also given during the padding of other samples, this samples was termed as 'control' sample with which the results of treated samples were compared as discussed in section 2.3.11, chapter 2.

4.3.3.1 Effect of N- substituted CHT treatment on appearance of cotton fabric

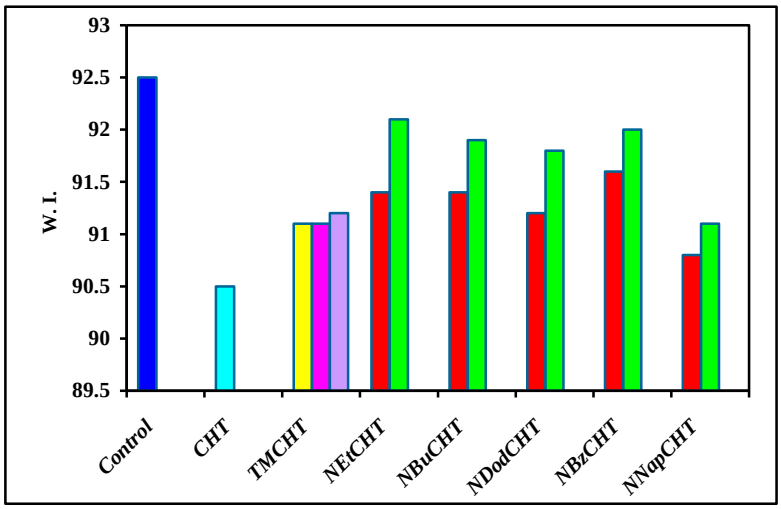
Analogous to the chitosan treatment, *N*- modified chitosans are believed to alter the surface characteristics of cotton fabrics. In context to this phenomenon, the CHT and *N*-substituted CHT derivatives treated cotton fabrics were evaluated for the whiteness, yellowness and brightness indices on computer colour matching system. The results are presented in Table 4.26 and Table 4.27 and in Figures 4.26, 4.27 & 4.28.

Table 4.26 Effect of *N*-Alkyl/Aryl CHT treatment on appearance of cotton fabric

Sample	DS, %	Conc in pad bath, g/L	Indices		
			WI	YI	BI
Control	-	-	92.5	2.6	84.6
CHT	-	2.5	90.9	3.3	81.6
		5	90.8	3.4	81.4
		10	90.5	4.7	80.6
N-Et CHT (1:2)	45.5	2.5	91.4	3.3	82.4
		5	90.9	3.3	81.6
		10	91.4	3.4	82.4
N-Bu CHT (1:2)	40.1	2.5	91.5	3.7	80.5
		5	91.8	3.3	82.6
		10	91.4	3.3	82.4
N-Dod CHT (1:4)	37.6	2.5	90.6	4.7	80.6
		5	91.1	3.5	82.5
		10	91.2	3.1	83.3
N-Bz CHT (1:4)	45.0	2.5	91.8	2.8	83.1
		5	91.7	3.3	82.6
		10	91.6	3.5	82.5
N-Np CHT (1:4)	37.6	2.5	91.8	2.8	83.1
		5	91.4	3.4	82.4
		10	90.8	3.4	81.4

Table 4.27 Effect of *N*-Alkyl/Aryl Q CHT derivatives treatment on appearance of cotton fabric

Sample	DQ, %	Conc in pad liquor, g/L	Indices		
			WI	YI	BI
Control	-	-	92.5	2.6	84.6
CHT	-	2.5	90.9	3.3	81.6
		5	90.8	3.4	81.4
		10	90.5	4.7	80.6
TMCHT1	13.4	2.5	92.0	2.811	83.0
		5	91.2	3.286	82.1
		10	91.1	3.5	82.5
TMCHT 2	22.0	2.5	91.6	2.8	83.0
		5	91.7	3.3	82.6
		10	91.1	3.5	82.2
TMCHT 3	50.9	2.5	91.8	2.8	83.1
		5	91.2	3.1	83.3
		10	91.2	3.4	82.4
N-Et Q CHT (1:2)	51.7	2.5	91.9	2.8	83.1
		5	91.5	3.3	82.4
		10	91.9	2.8	83.1
N-Bu Q CHT (1:2)	47.5	2.5	92.2	2.6	83.3
		5	92.0	2.6	83.0
		10	91.8	2.8	83.0
N-Dod Q CHT (1:4)	45.1	2.5	91.3	3.3	82.4
		5	91.6	3.3	82.4
		10	91.8	3.3	82.6
N-Bz Q CHT (1:4)	41.4	2.5	92.3	2.6	83.1
		5	92.1	2.6	82.7
		10	92.0	2.9	82.7
N-Np Q CHT (1:4)	40.0	2.5	92.2	2.7	83.3
		5	91.8	3.3	82.6
		10	91.1	3.3	82.1

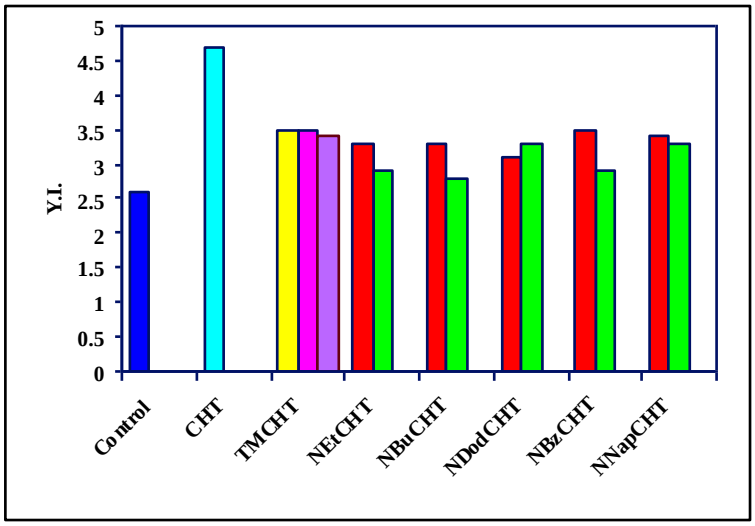


Control | TMCHT1 treated | TMCHT3 treated | *N*-Alky/Aryl Q CHT treated

CHT treated | TMCHT2 treated | *N* – Alky/Aryl CHT treated

DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40; WI: 10 deg/D65/Hunterlab

Figure 4.26 Effect of *N*-Sub CHT treatment on whiteness of cotton fabric

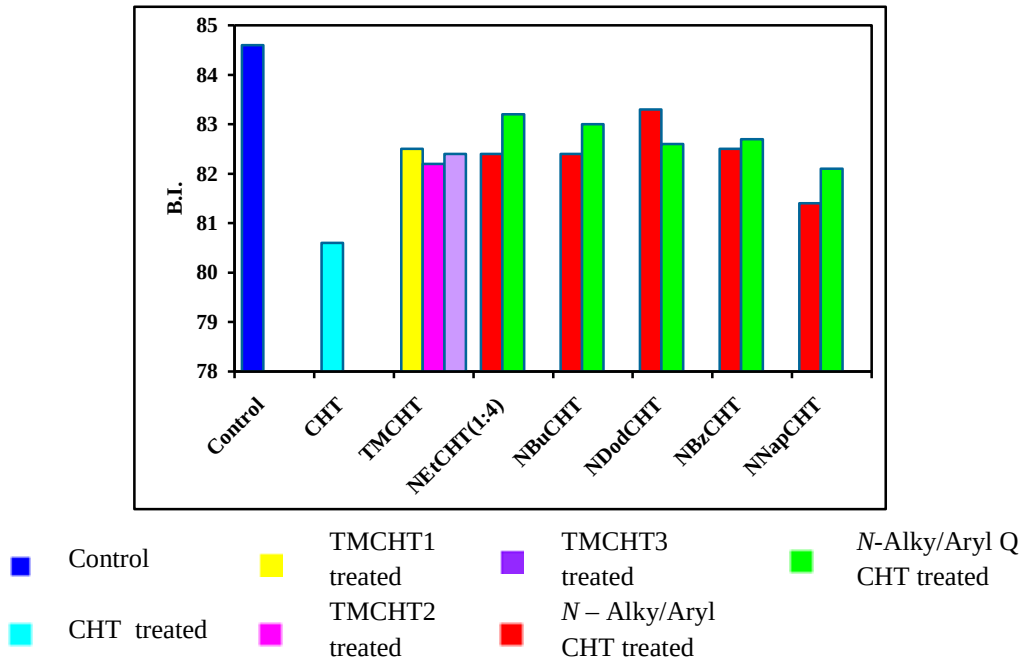


Control | TMCHT1 treated | TMCHT3 treated | *N*-Alky/Aryl Q CHT treated

CHT treated | TMCHT2 treated | *N* – Alky/Aryl CHT treated

DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40; YI: 2 deg/C/ASTM D 1925

Figure 4.27 Effect of *N*-Sub CHT treatment on yellowness of cotton fabric



DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40; BI: 2 deg/C/TAPPI 452/ISO 2470

Figure 4.28 Effect of *N*-Sub CHT treatment on brightness of cotton fabric

It was observed from Table 4.26 and Table 4.27 that the appearance of the *N*-substituted CHT and their quaternized derivatives were satisfactory. With increase in concentrations of these derivatives, the appearance was very slightly affected and the differences were nominal. Figures 4.26, 4.27 & 4.28 revealed that the indices were decreased sharply due to CHT treatment and then improved due to N-substitution and then further improved by quaternization.

4.3.3.2 Effect of N- substituted CHT treatment on stiffness of cotton fabric

Besides appearance, the appeal of cotton fabric is characterized by another inherent quality i.e. handle or feel which is popularly known as 'cotton-feel'. Treatment of CHT on cotton fabric, as illustrated in chapter 2, was found to impart undesired stiffness and impaired its handle. In order to sustain the inherent natural feel, the fabric was treated with *N*- alkyl and *N*-aryl CHT and their quaternized derivatives. The effect of chain length of *N*-alkyl substituent and the molecular size of *N*-aryl substituents on CHT

on the performance of cotton in context to handle is presented in Table 4.28. Very slight increase in stiffness was noticed due to the treatment of *N*-alkyl and *N*-aryl chitosan as against the parent chitosan treated fabrics. With increase in chain length of alkyl substituent the stiffness was gradually decreased indicating the improvement in handle. Almost similar trend was noticed in case of *N*-aryl substituted CHT derivatives. Quaternization of these *N*- substituted CHT derivatives, however, resulted into a slight introduction of stiffness. In case of TMCHT derivatives, the bending length was minimum at lower DQ and increased progressively with increase in DQ, nevertheless to a very small extent.

Table 4.28 Effect of *N*- sub CHT treatment on stiffness of cotton fabric

Bending Length, cm							
***N*-Alkyl/Aryl CHT treated fabric**				***N*-Alkyl/Aryl Q CHT treated fabric**			
Sample	**DS, %**	**Warp**	**Weft**	**Sample**	**DQ, %**	**Warp**	**Weft**
Control	-	2.05	1.68	Control	-	2.05	1.68
CHT	-	3.70	2.74	CHT	-	3.70	2.74
TMCHT1	-	-	-	TMCHT1	13.4	2.21	1.60
TMCHT2	-	-	-	TMCHT2	22.0	2.32	1.70
TMCHT3	-	-	-	TMCHT3	50.9	2.49	1.85
N-Et CHT (1:2)	45.5	2.46	1.70	N-Et Q CHT (1:2)	51.7	2.50	1.73
N-Bu CHT (1:2)	40.1	2.48	1.72	N-Bu Q CHT (1:2)	47.5	2.42	1.86
N-Dod CHT (1:4)	37.6	2.36	1.68	N-Dod Q CHT (1:4)	45.1	2.54	1.76
N-Bz CHT (1:4)	45.0	2.32	1.62	N-Bz Q CHT (1:4)	41.4	2.52	1.76
N-Np CHT (1:4)	37.6	2.38	1.60	N-Np Q CHT (1:4)	40.0	2.32	1.60

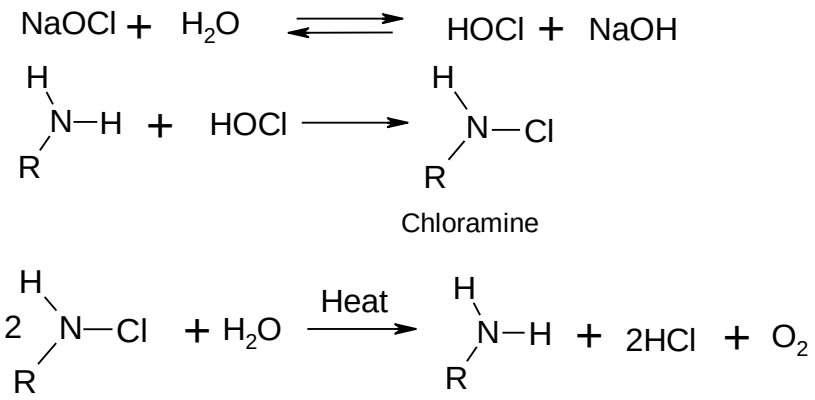
Conc of CHT derivatives in pad liquor 10g/L

The reduction in stiffness may be ascribed to the lubricating action of long chain hydrocarbon of alkyl group [2, 73] and also to the depolymerization of main CHT chain during *N*- substitution and quaternization processes as observed from the fall in intrinsic viscosity as discussed elaborately in proceeding chapter (Chapter 5). The feel of the fabric, evaluated by finger inspection, was very satisfactory. The fabric smoothness was

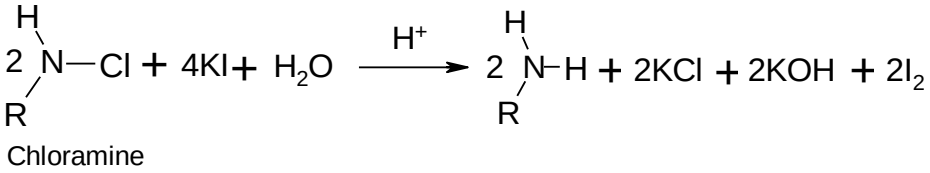
improved with increase in molecular size of *N*-substituents. This may again attributed to the softness effect of hydrocarbon side groups.

4.3.3.3 Effect of N-substituted CHT treatment on chlorine retention property

The appearance of cotton fabric treated with compounds containing free -NH- groups such as aminoplasts, cationic softeners, amino silicones etc is severely affected due to yellowness caused by chlorine retention. This property also of free -NH- group containing compounds leads to tremendous loss in fibre strength, produces rancid/bad odour and is toxic due to the formation of chloramines as shown in scheme 4.13. Since chitosan belongs to polycation containing pendant amino groups which are sites for chlorine retention. The object of *N*- modification, in part, in present work was to reduce the chlorine retention problem. The process of yellowing, however, was a very slow. In order to intensify the yellowness for faster evaluation, the samples were treated with solution containing potassium iodide and acetic acid where in the formed chloarmie reacts with acidic potassium iodide to liberate iodine as shown in scheme 4.14 [1]. Effect of quaternization of *N*- substituted CHT on appearance and tensile strength of cotton fabric due to chlorine retention is illustrated in Table 4.29 and graphically in Figure 4.29 and Figure 4.30.



Scheme 4.13 Reactions involved in chlorine retention



Chloramine

Scheme 4.14 Reaction of chloramine with potassium iodide

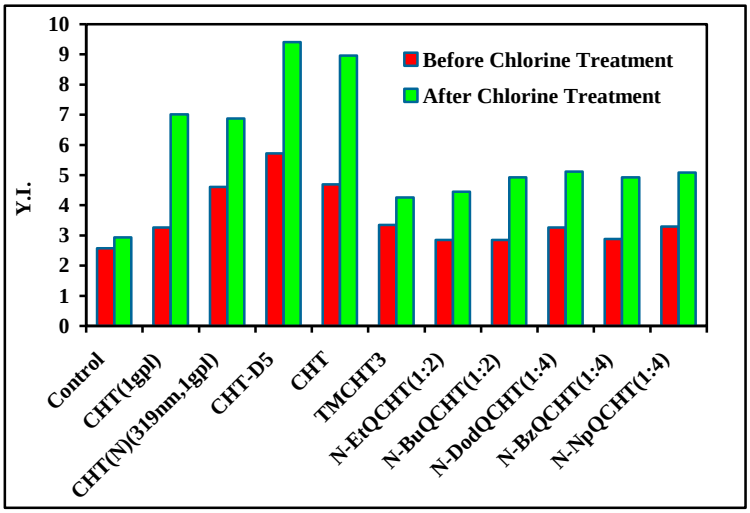
Table 4.29 Effect of different CHT and *N*- sub CHT derivatives treatment on chlorine retention on cotton fabric

Sample	Conc in pad bath, g/L	YI		Tenacity, g/tex		
		Before chlorine treatment	After chlorine treatment	Before chlorine treatment	After chlorine treatment	Loss in strength (%)
Untreated cotton	-	-	-	23.33	21.18	9.22
Control	-	2.6	2.9	20.87	18.63	10.73
CHT	1	3.3	7.0	20.48	17.48	14.63
CHT(N)	1	4.6	6.9	25.61	20.81	18.74
CHT-D5	10	5.7	9.4	22.08	16.74	24.18
CHT	10	4.7	9.0	21.77	15.64	28.16
TMCHT3	10	3.4	4.3	21.18	19.71	6.94
N-Et Q CHT(1:2)	10	2.9	4.5	21.68	20.16	7.01
N-Bu Q CHT(1:2)	10	2.9	4.9	20.14	18.77	6.87
N-Dod Q CHT(1:4)	10	3.3	5.1	21.36	19.69	7.81
N-Bz Q CHT(1:4)	10	2.9	4.9	21.81	20.05	8.05
N-Np Q CHT(1:4)	10	3.3	5.1	19.92	18.33	7.96

CHT (N): Particle size 319.4nm, Mol wt: CHT-D5 =11986, CHT= 135,839, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

The results shown in Table 4.29 and in Figures 4.29 & 4.30 clearly revealed that the cotton fabric treated with different grades of CHT without *N*-modification was susceptible to chlorine damage. With increase in concentration of CHT, the yellowness problem and tensile strength losses were found to be increased. The change in molecular

weight of chitosan showed some anomaly. The appearance of CHT-D5 (low mol wt chitosan) was poorer than the CHT (high mol wt chitosan). This may be attributed to the yellowness imparted to CHTD 5 during depolymerization process itself as observed from Y.I. of CHTD5 before chlorine treatment in the Figures 4.29. The reduction in particle size e.g. CHT (N) showed greater susceptibility to chlorine damage than the normal CHT. This was expected, because smaller particle sizes have greater reactivity and also penetrate more in to the fibre structure leading to more proximity of fibre for such degradation reactions. The *N*-substitution and quaternization of CHT were found to overcome the chlorine retention problem substantially. The yellowness imparted and the fibre strength losses were nominal. No definite trend was observed in context to the chain length or molecular size of substituents. However, trimethyl chitosan derivative was found to be somewhat more resistant to chlorine damage than the *N*-alkyl or *N*-aryl quaternized CHT derivatives.



Conc in pad bath 10 g/L, CHT (N): Particle size 319.4nm, Mol wt: CHT-D5 =11986, CHT= 135,839, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.29 Effect of *N*-Sub CHT treatment on yellowness of cotton fabric due to chlorine retention

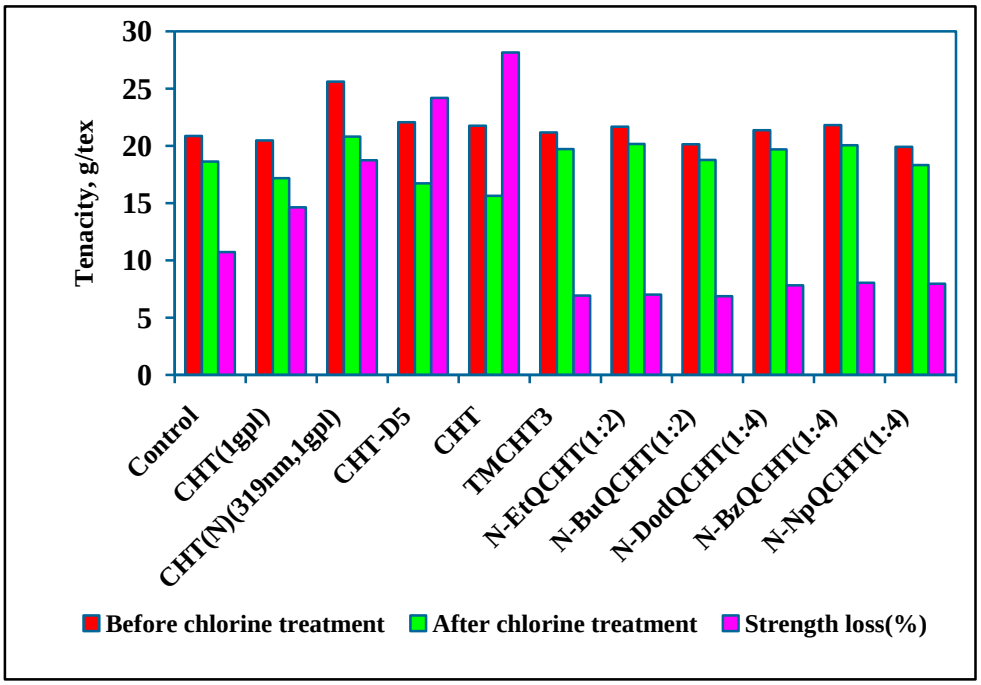


Figure 4.30 Effect of *N*-Sub CHT treatment on fibre strength of cotton due to chlorine retention

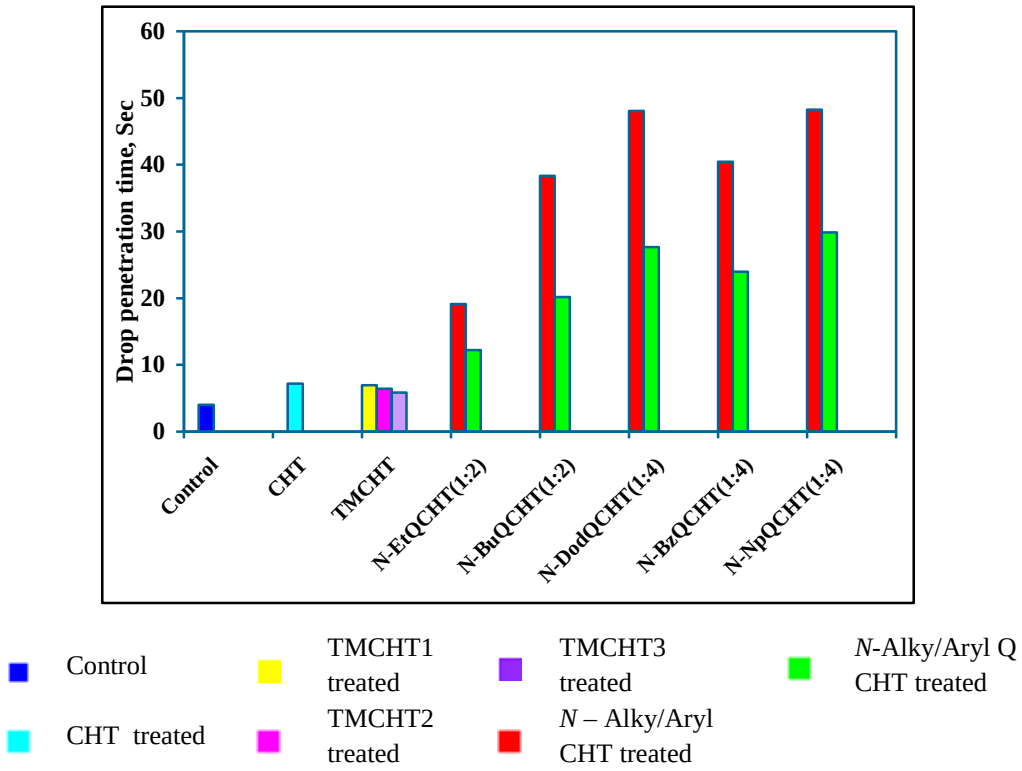
4.3.3.4 Effect of N- substituted CHT treatment on absorbency of cotton fabric

The absorbency of *N*-alkyl and *N*-aryl CHT and their quaternized derivatives treated cotton fabric were measured by drop penetration method. The results are presented in Table 4.30 and graphically in Figure 4.31.

Table 4.30 Effect of *N*-sub CHT treatment on absorbency of cotton fabric

***N*-Alkyl/Aryl CHT treated fabric**			***N*-Alkyl/Aryl Q CHT treated fabric**		
Sample	**DS, %**	**Absorbency, Sec**	**Sample**	**DQ, %**	**Absorbency, Sec**
Control	-	4.0	Control	-	4.0
CHT	-	7.2	CHT	-	7.2
TMCHT1	-	-	TMCHT1	13.4	7.0
TMCHT2	-	-	TMCHT2	22.0	6.4
TMCHT3	-	-	TMCHT3	50.9	5.8
N-Et CHT (1:2)	45.5	19.1	N-Et QCHT (1:2)	51.7	12.2
N-Bu CHT (1:2)	40.1	38.3	N-Bu Q CHT (1:2)	47.5	20.2
N-Dod CHT (1:4)	37.6	48.1	N-Dod QCHT(1:4)	45.1	27.7
N-Bz CHT (1:4)	45.0	40.5	N-Bz QCHT(1:4)	41.4	24.0
N-Np CHT (1:4)	37.6	48.3	N-Np QCHT(1:4)	40.0	29.8

Conc of CHT derivatives in pad liquor 10g/L



DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.31 Effect of *N*-sub CHT treatment on absorbency of cotton fabric

The absorbency was affected due to alkyl or aryl substituents and was decreased with increase in molecular size of substituents. Quaternization of CHT and *N*-Sub CHT derivatives was found to improve the absorbency of treated fabric substantially. In case of TMCHT, the absorbency was increased progressively with increase in DQ. The hydrophobicity imparted by *N*-alkyl or aryl groups was overcome by the quaternization yet the effect due to hydrophobic substituents did persist. Quaternization results the amino groups in to quaternary ammonium salts which are permanently in ionic form. These cat ions can easily get surrounded by water molecules due to ion-dipole forces [22, 74] and thus increase the absorbency.

4.3.5.5 Effect of N- substituted CHT treatment on direct dyeing of cotton fabric

A significant improvement in dye uptake due chitosan treatment of cotton fabric has been revealed in 2.3.13.1, chapter 2. The pendant amino groups of chitosan, however,

are not completely in ionic form in neutral or alkaline bath. The cationic charge on chitosan can only be developed when protonated, as in acidic medium. Cotton dyeing, however, conventionally is carried out in alkaline dye baths and therefore complete exhaustion of such dyes on chitosan treated fabric is not achieved. In view of this, a permanent cationic charge with improved hydrophilicity on the chitosan macromolecule was developed by quaternization protocol.

Table 4.31A Effect of *N*-sub CHT treatment on direct dyeing of cotton fabric

Sample	**Conc in pad liquor, g/L**	**K/S values**			
		C. I. Direct Red 81		**C. I. Direct Blue 71**	
		Conventional dye bath	**Salt free dye bath**	**Conventional dye bath**	**Salt free dye bath**
Control	-	7.73	5.86	7.41	5.48
CHT	2.5	9.41 *[22]*		9.60 *[29]*	
	5	10.16 *[32]*		10.81 *[46]*	
	10	10.97 *[42]*	9.89	12.42 *[68]*	10.78
TMCHT1	2.5	9.94 *[29]*		9.94 *[34]*	
	5	10.86 *[41]*		11.58 *[56]*	
	10	11.39 *[48]*	10.37	12.06 *[63]*	10.86
TMCHT2	2.5	10.63 *[38]*		10.14 *[37]*	
	5	11.39 *[48]*		11.69 *[58]*	
	10	12.01 *[56]*	11.29	12.28 *[66]*	11.42
TMCHT3	2.5	11.47 *[49]*		10.58 *[43]*	
	5	11.86 *[54]*		11.91 *[61]*	
	10	12.40 *[61]*	11.90	12.73 *[72]*	11.97

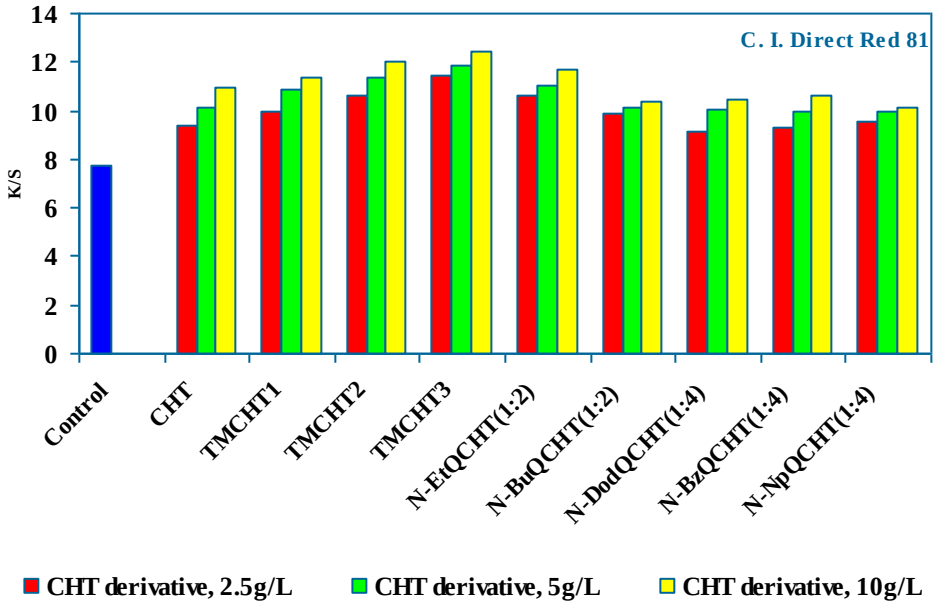
Dye 1% o.w.m, Values in brackets indicate the change in colour value from control

Table 4.31B Effect of *N*-sub CHT treatment on direct dyeing of cotton fabric

Sample	Conc in pad liquor, g/L	K/S values			
		C. I. Direct Red 81		C. I. Direct Blue 71	
		Conventional dye bath	Salt free dye bath	Conventional dye bath	Salt free dye bath
Control	-	7.73	5.86	7.41	5.48
N-Et QCHT (1:2)	2.5	10.66 *[38]*		10.43 *[41]*	
	5	11.01 *[43]*		11.84 *[60]*	
	10	11.70 *[52]*	10.89	12.36 *[67]*	11.37
N-Bu QCHT (1:2)	2.5	9.86 *[28]*		10.36 *[40]*	
	5	10.09 *[31]*		10.95 *[48]*	
	10	10.39 *[35]*	10.08	11.03 *[49]*	10.19
N-Dod Q CHT (1:4)	2.5	9.16 *[19]*		10.06 *[36]*	
	5	10.01 *[30]*		10.51 *[42]*	
	10	10.47 *[36]*	10.16	10.43 *[41]*	9.60
N-Bz QCHT (1:4)	2.5	9.32 *[21]*		9.77 *[32]*	
	5	9.93 *[29]*		10.21 *[38]*	
	10	10.63 *[38]*	10.31	10.51 *[42]*	9.72
N-Np QCHT (1:4)	2.5	9.55 *[24]*		9.77 *[32]*	
	5	9.94 *[29]*		9.92 *[34]*	
	10	10.16 *[32]*	9.86	10.21 *[38]*	9.45

Dye: 1% o.w.m., Values in brackets indicate the change in colour value from control,
DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

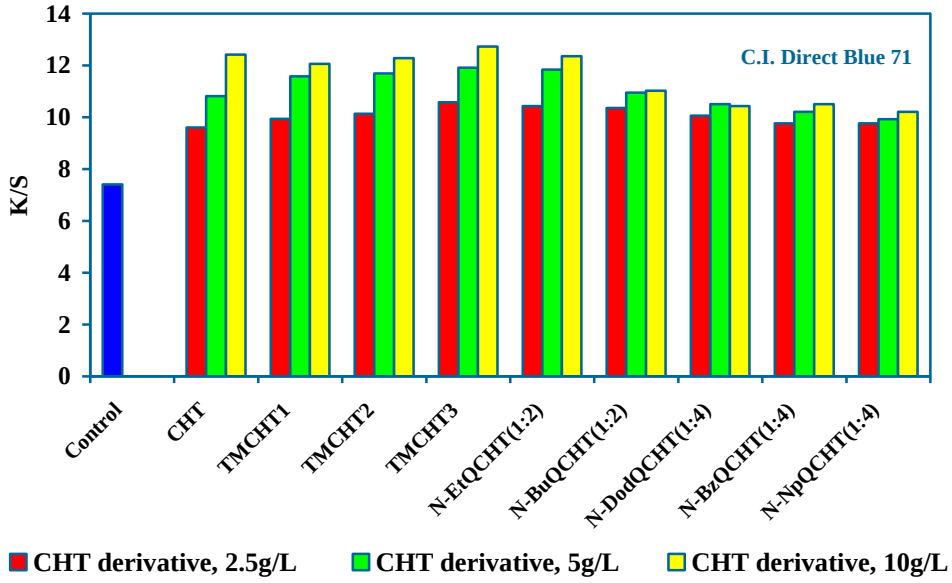
Thus the effect of quaternized *N*- alkyl and *N*-aryl CHT derivatives on dyeing behaviour of cotton fabric was studied. The effects of different *N*- modified chitosans treatment on direct dyeing of cotton fabric, measured in terms of K/S, are shown in Table 4.31(A&B) and graphically in the Figures 4.32 and 4.33 respectively; and their washing fastnesses are presented in Table 4.32.



Dye (C. I. Direct Red 81)1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.32 Effect of *N*-sub CHT treatment on direct dyeing of cotton fabric

It was observed from Table 4.31(A & B) and corresponding Figure 4.32 and Figure 4.33 that the dye uptake on cotton fabric for both the dyes increased with increase in concentration of each CHT derivative treatment. The degree of quaternization also influenced the dyeability of treated fabric. The dyeability was increased progressively with DQ for TMCHT. However, for a given degree of substitution, the dye uptake was declined with increase in alkyl chain length and aryl groups. As the quaternization imparts permanent cations on CHT can establish ionic linkages with anionic groups on direct dyes. Thus the synergistic effect of ionic linkages between quaternized CHT and dye together with usual dye- fibre and Dye-TMCHT bonds such as H-bonds and other physical forces showed the enhanced dye uptake for quaternized CHT derivative treated fabrics.



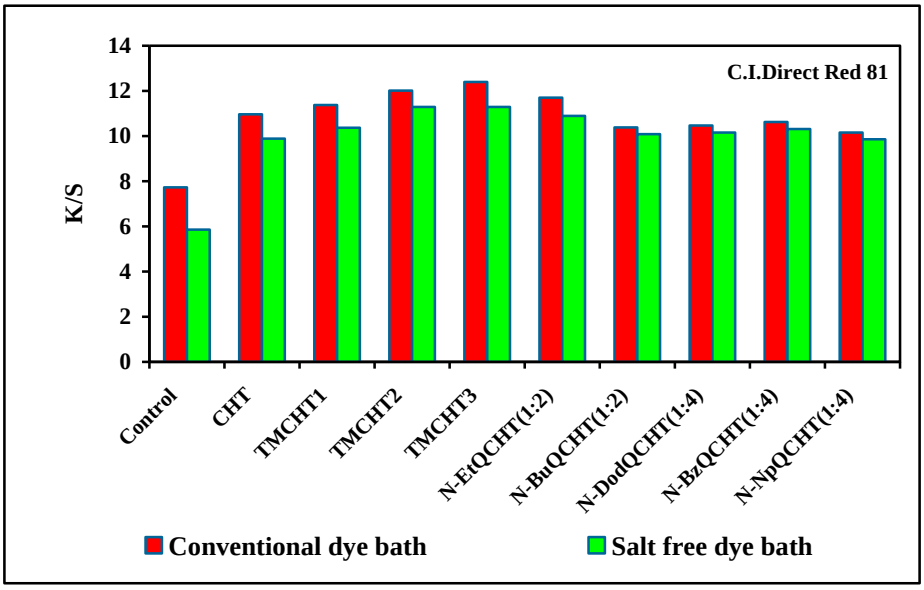
Dye (C. I. Direct Blue 71)1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.33 Effect of *N*-sub CHT treatment on direct dyeing of cotton fabric

With increase in chain length of *N*- alkyl substituent by methylene spacer and molecular size of *N*-aryl substituent by benzene rings, hydrophobic barrier between the dye and the fibre is created due to the bulkier side groups showing declined trend of dye uptake. The effect of hydrophobicity was more prominently seen with *N*- Dod Q CHT and *N*-Np Q CHT derivatives treated fabrics. The higher hydrophobicity due to these derivatives treatment has also been verified from absorbency data from Table 4.30 or Figure 4.31. The decreased dyeability due to hydrophobic substituents was overcome with quaternization of the *N*- substituted CHT derivatives. Thus for lower *N*- substituted CHT derivatives the dyeing was governed by degree of quaternization showing enhanced dye uptake while for higher derivatives the dyeing was governed by two diverse phenomena namely, one decreased dyeability due to bulkier substituents and second the increased dyeability due to quaternary groups.

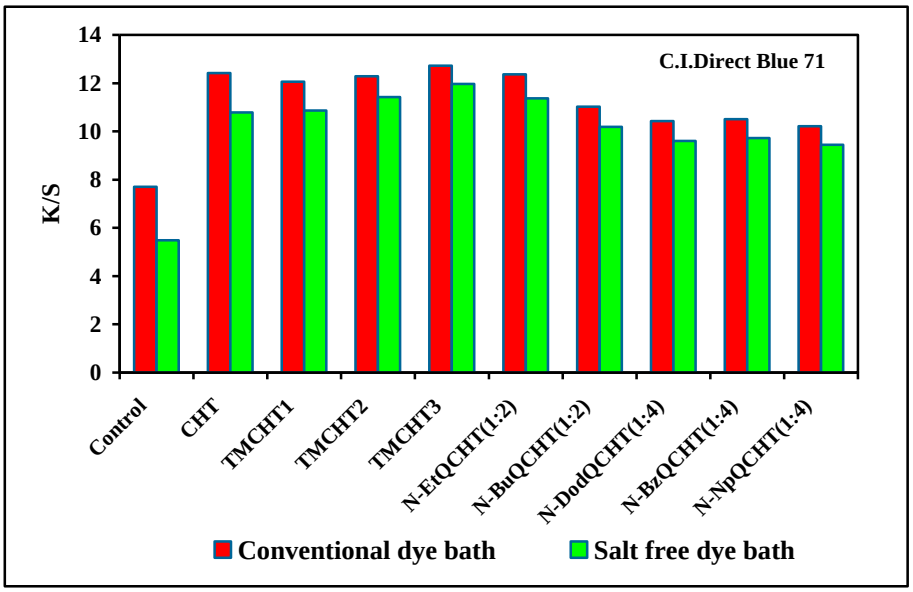
In order to understand the attributes of cations of quaternary ammonium groups for enhanced dyeability, the dyeing results of salt free dye bath were compared with that of conventional dye bath as illustrated in Table 4.31 (A&B) and in Figures 4.34, 4.35 and

4.36. It was found that the difference in dye uptake (colour difference) between conventional and salt free dye bath samples was sharply dropped due to quaternization i.e. diminishing the role of electrolyte in dye bath in case of quaternized CHT treated fabrics. Thus, according the theory of cotton dyeing [75] the fibre acquires -ve zeta potential that is responsible for repulsion of anionic direct dyes. The added salt in dye bath dissipates the -ve charge due the adsorption of inorganic +ve ions facilitating the adsorption of direct dyes on fibre by virtue of its affinity. This phenomenon of charge dissipation is now performed by cat ions of quaternized CHT derivatives. Thus these cations serve two purposes i.e. the -ve charge dissipation on fibre surface and the formation of salt linkages with dye.



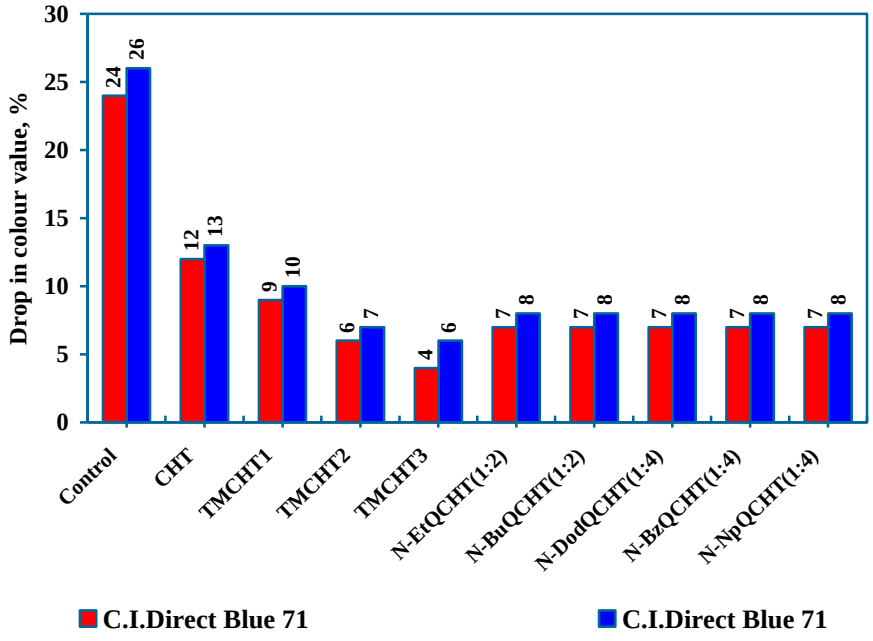
N-Alkyl/Aryl Q CHT in pad liquor 10 g/L, Dye (C. I. Direct Red 81) 1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.34 Effect of dye bath condition on direct dyeing of *N*-Sub CHT treated cotton fabric



N- Alkyl/Aryl Q CHT in pad liquor 10 g/L, Dye (C. I. Direct Red 81) 1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.35 Effect of dye bath condition on direct dyeing of *N*-Sub CHT treated cotton fabric



N- Alkyl/Aryl Q CHT in pad liquor 10 g/L, Dye 1% o.w.m

Figure 4.36 Drop in colour value of salt free dyeing from conventional dye bath in direct dyeing of *N*-Sub Q CHT treatment of cotton fabric

The influence of quaternization of CHT and *N*-substituted CHT on washing fastness of direct dyes is enumerated in Table 4.32. It was observed that the fastness was slightly improved with increase in DQ of TMCHT treated samples but was again affected due to *N*- alkyl chain length or *N*-aryl groups. The attachment of dye molecules to quaternary ammonium groups on TMCHT is comparatively stronger due to their ionic interaction and therefore is firmly retained by the TMCHT treated fibres. The hydrophobic large side groups due to *N*- substitution weaken the attachments between dye and quaternary groups due to pushing of dye away from the sites resulting into poor fastness. The overall fastness washing, however, is determined by the simultaneous effects of attachment of dye with the dye sites on fibre and CHT derivatives and the interaction between the CHT derivative sand the fibre.

Table 4.32 Effect of *N*-sub CHT treatment on washing fastness of direct dyed cotton fabrics

Sample	**Conc in pad bath, g/L**	**Washing fastness ratings**			
		C. I. Direct Red 81		**C. I. Direct Blue 71**	
		Change in Color	**Staining**	**Change in Color**	**Staining**
Control	-	3	3	4-5	3-4
CHT	5	3	2-3	4-5	3-4
	10	3-4	2-3	4-5	3-4
TMCHT1	5	3-4	3	4-5	3-4
	10	3-4	3	4-5	3-4
TMCHT2	5	3-4	3-4	4-5	3-4
	10	3-4	3-4	4-5	3-4
TMCHT3	5	4	3-4	4-5	4
	10	4-5	3-4	4-5	4
N-Et QCHT (1:2)	5	3-4	3	4-5	4
	10	3-4	3	4-5	4
N-Bu QCHT (1:2)	5	3	2-3	3-4	3-4
	10	2-3	2-3	3-4	3-4
N-Dod QCHT (1:4)	5	2	2-3	3	3-4
	10	2	2	3	3-4
N-Bz QCHT (1:4)	5	2-3	2-3	3-4	3-4
	10	2-3	2-3	3-4	3-4
N-Np QCHT (1:4)	5	2-3	2-3	3-4	3-4
	10	2-3	2-3	3-4	3

4.3.3.6 *Effect of N- substituted chitosan treatment on colour depth of direct dyed cotton fabric*

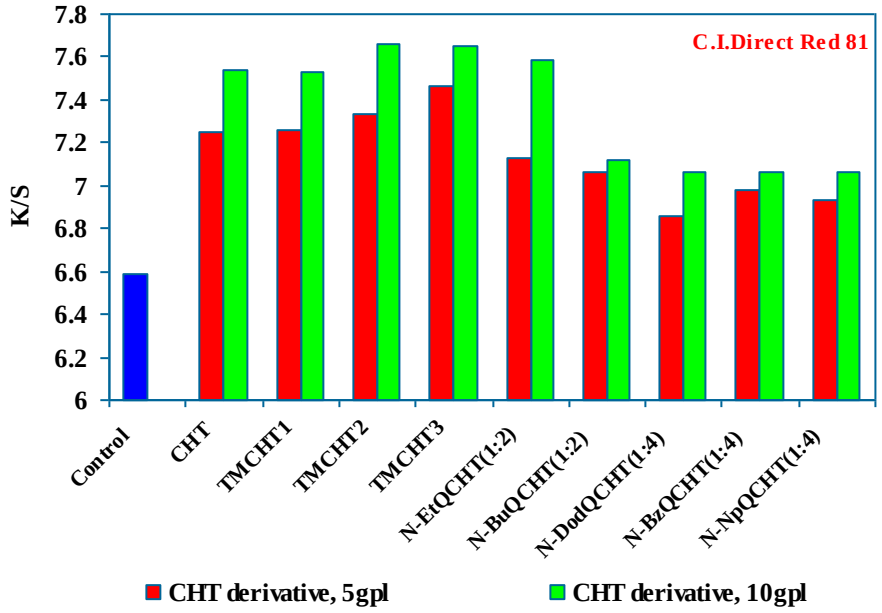
It was observed from previous discussion that the *N*-substitution of CHT treatment improved the handle of the fabric substantially. It is also anticipated that such modifications play important role in on other properties of treated fabrics such as wrinkle recovery, antibacterial and soil release and hence these products can be employed as a textile finishing auxiliary. Treatment of *N*- modified chitosan, like parent chitosan as discussed in chapter 2, can alter the colour value and fastness properties of dyed fabrics. The effect of post dyeing treatment of different *N*- substituted CHT derivatives direct dyed cotton fabric are presented in Table 4.33 and Table 4.34 and graphically in Figures 4.37 and 4.38. It was observed that the two dyes respond differently for the CHT derivative treatments. The C.I. Direct Red 81dyed fabrics showed improved intensity of colour than that of C.I. Direct Blue 71dyed samples. The colour depth of both the shades was found to be increased with increase in concentration of CHT derivatives treatments. The maximum intensity, in both the dyes, was observed when the dyed fabrics were treated with TMCHT3. It means higher the degree of quaternization; the more will be the shade darker. The apparent changes in shade may be attributed to the migration of dye from fibre phase to CHT derivatives phase. The quaternary ammonium sites being permanently cat ionic and responsible for hydrophilicity, can readily interact with anions ($-SO_3^-$ groups) of dye. As the molecular size of substituent is increased the probability of such interactions is lowered and hence the extent of migration of dye towards CHT derivative layer is lowered. Further, the easily washable C.I. Direct Red 81dye is migrated to greater extent from fabric to CHT derivative layer during pad application and then drying. The washing fastness of post dyeing CHT derivative treatment was found to be slightly improved. This may be attributed to the complex formation between dye and the CHT derivatives through salt linkages.

Table 4.33 Effect of *N*-Sub CHT treatment on colour depth of direct dyed cotton fabrics (Post dyeing treatment)

Sample	Conc in pad liquor, g/L	C.I. Direct Red 81		C.I. Direct Blue 71	
		K/S value	*Colour change, %	K/S value	*Colour change, %
Control (Dyed)	-	6.59	-	7.29	-
CHT	5	7.25	9	6.83	-7
	10	7.54	14	7.31	3
TMCHT1	5	7.26	10	6.94	-5
	10	7.53	14	7.52	3
TMCHT2	5	7.33	11	7.37	1
	10	7.66	16	7.52	3
TMCHT3	5	7.46	13	7.61	3
	10	7.65	16	7.67	5
N-Et QCHT (1:2)	5	7.13	8	7.45	2
	10	7.59	15	7.74	6
N-Bu QCHT (1:2)	5	7.06	7	7.40	1
	10	7.12	8	7.53	3
N-Dod QCHT (1:4)	5	6.86	4	7.23	-1
	10	7.06	7	7.45	2
N-Bz QCHT (1:4)	5	6.98	6	7.15	-2
	10	7.06	7	7.38	1
N-Np QCHT (1:4)	5	6.93	5	7.16	-2
	10	7.06	7	7.30	--

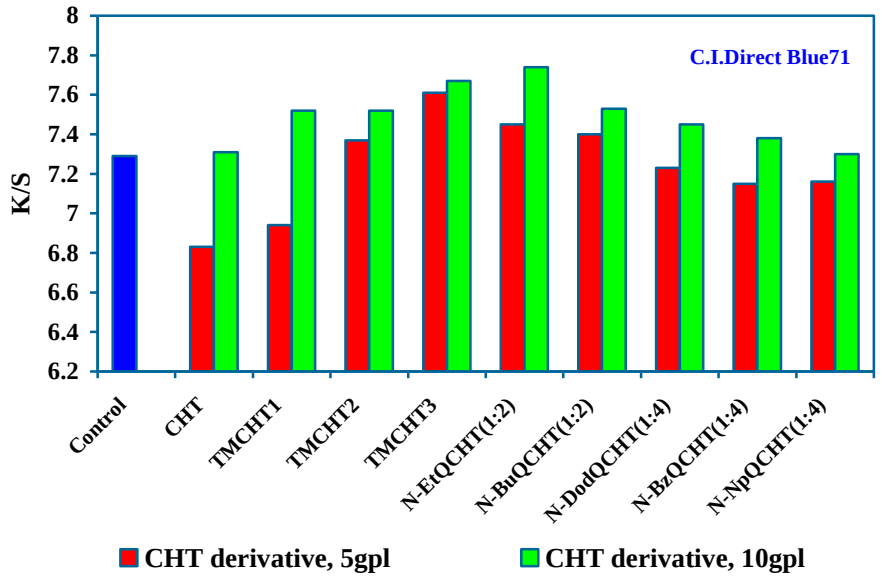
Dye 1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

**Colour change from dyed control sample*



Dye (C. I. Direct Red 81) 1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.37 Effect of *N*-Sub CHT treatment on colour depth of direct dyed cotton fabrics



Dye (C. I. Direct Blue 71) 1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.38 Effect of *N*-Sub Q CHT derivatives treatment on colour depth of direct dyed cotton fabrics

Table 4.34 Effect of *N*-sub CHT treatment on washing fastness of direct dyed cotton fabric

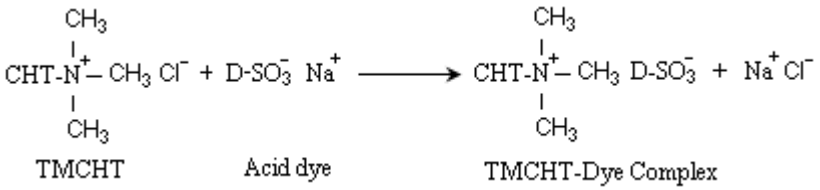
Sample	Washing Fastness			
	CI Direct Red 81		CI Direct Blue 71	
	Change in Colour	Staining	Change in Colour	Staining
Control (Dyed)	3	3	4-5	3
CHT	3-4	2-3	4	4-5
TMCHT1	3-4	2-3	4	4
TMCHT2	3-4	3	4-5	4
TMCHT3	4-5	3-4	4-5	4-5
N-Et QCHT (1:2)	3	3	4	4
N-Bu QCHT (1:2)	3-4	3	4	4-5
N-Dod QCHT (1:4)	3-4	3	4-5	4
N-Bz QCHT (1:4)	3-4	3	4-5	4-5
N-Np QCHT (1:4)	3-4	3	4-5	4

Dye: 1% o.w.m, Conc of CHT derivatives in pad bath 10 g/L, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

4.3.3.7 Effect of N- substituted CHT treatment on acid dyeing

Attributing to cationic nature of CHT derivatives, the work was extended to investigate the effect on dyeability of CHT derivatives treated cotton fabric towards acid dye, which is non dyeable towards normal cotton. The results are presented in Table 4.35 and in Figure 4.39. It was revealed from these demonstrations that the CHT and quaternized CHT derivatives treated cotton fabrics dyed substantially with C.I. Acid Blue158 as against only a tint on control. Since quaternary ammonium site of TMCHT and quaternized *N*-Sub CHT should form ionic linkages with stoichiometric amount of anionic acid dyes as illustrated by the scheme 4.15 in neutral dye bath. The CHT derivatives treated fabric in acidic dye bath showed almost similar extent of exhaustion of acid dye except little decline in higher derivatives. In acidic medium, besides quaternary ammonium sites, almost all remaining amino groups are believed to get protonated and therefore a similar dye uptake was observed as expected. Little decrease in dye uptake in higher CHT derivative treated fabric may be due to the steric hindrance of bulkier side groups. In neutral dye bath, the dyeing phenomenon follows the ion exchange reaction of

scheme 4.15.Therefore a progressive increase in dye uptake corresponding to degree of quaternization (stoichiometry) was observed.

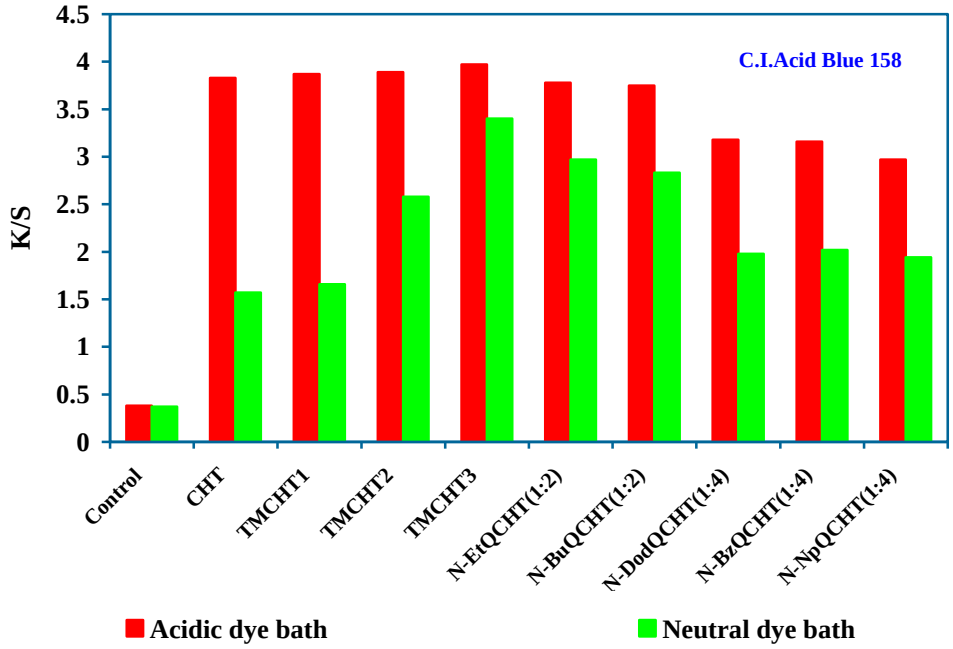


Scheme 4.15 Reaction trimethyl chitosan ammonium chloride salt with acid dye

Table 4.35 Effect of *N*-Sub CHT treatment on dyeing with C.I. Acid Blue158

Sample	**Conc in pad bath, g/L**	**K/S Value**	
		Acidic Dye bath	**Neutral Dye bath**
Control	-	0.38	0.37
CHT	5	2.10	0.79
	10	3.83	1.57
TMCHT1	5	2.15	1.06
	10	3.87	1.66
TMCHT2	5	2.13	1.34
	10	3.89	2.58
TMCHT3	5	2.19	1.76
	10	3.97	3.40
N-Et QCHT (1:2)	5	2.08	1.17
	10	3.78	2.97
N-BuQCHT (1:2)	5	2.07	1.07
	10	3.75	2.83
N-Dod QCHT (1:4)	5	2.05	0.91
	10	3.18	1.98
N-Bz QCHT (1:4)	5	1.99	0.97
	10	3.16	2.02
N-Np QCHT (1:4)	5	1.98	0.85
	10	2.97	1.94

Dye: 2% o.w.m, DQ(%): TMCHT1=13.4,TMCHT2=22,TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40



Dye (C.I. Acid Blue158) 2% o.w.m, Conc in pad bath 10 g/L, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.39 Effect of *N*-Sub CHT treatment on dyeing with acid dye

4.3.3.8 Effect of N-substituted CHT treatment on wrinkle recovery properties of cotton fabric

The chitosan treatment was found to impair the wrinkle recovery property of cotton fabric. The problem of creasing was attributed, mostly, to surface coating of non elastic stiff film that deform easily when pressed. Indeed, the wrinkle recovery property governed is mainly by the cross linking phenomenon that is not taking place with/by CHT treatment. In order to understand the influence of quaternization and *N*- substitution of CHT by varying length of alkyl chain and molecular size of aryl groups to the resiliency of cotton fabrics, the CRA of CHT derivative treated fabrics against commercial cross linking agents was evaluated. The performances of these treated samples are demonstrated in Table 4.36 and Table 4.37. It was observed from these tables that the resiliency improved nevertheless did not reach the commercial requirements of DMDHEU. Addition of commercial cross linking agents to the pad bath formulation is recommended.

Table 4.36 Wrinkle recovery property of *N*-sub CHT treated cotton fabric

Sample	CRA^0 of fabric treated at:	
	5 g/L	10 g/L
CHT	140	125
TMCHT1	171	167
TMCHT2	172	175
TMCHT3	177	174
N-Et QCHT (1:2)	169	167
N-Bu QCHT (1:2)	172	175
N-Dod QCHT (1:4)	175	176
N-Bz QCHT (1:4)	167	166
N-Np QCHT (1:4)	164	161

CRA of Control: 161^0, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9;
DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5,
N-Dod Q CHT (1:4) = 37.6/45.1, N-Bz Q CHT (1:4) = 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Table 4.37 Wrinkle recovery property of DMDHEU treated cotton fabric

DMDHEU, g/L	CRA^0
Control	161
20	180
40	207
60	215
80	226
100	233

4.3.3.9 Effect of N- substituted CHT treatment on soiling behaviour of cotton fabric

Besides creasing tendency, the appeal of garments is also severely hampered due to another phenomenon, namely soiling. It arises due deposition of different kinds of undesired impurities termed as 'soil' through various agencies such as contact transfer, medium transfer, electrostatic attraction etc as described in literature [73, 76-79]. Of the particular concern with the oily soil that is most commonly observed, the oil forms a thin film around individual fibre. This film leads to increased build-up with successive soilings and serves as adhesive for particulate matter, thus greatly affecting the cloth

appearance. The oily soil most often deposited on garments is human sebum which is a complex mixture of lipids.

Table 3.38 Effect of different CHT and *N*- sub CHT treatment on soiling of cotton fabric

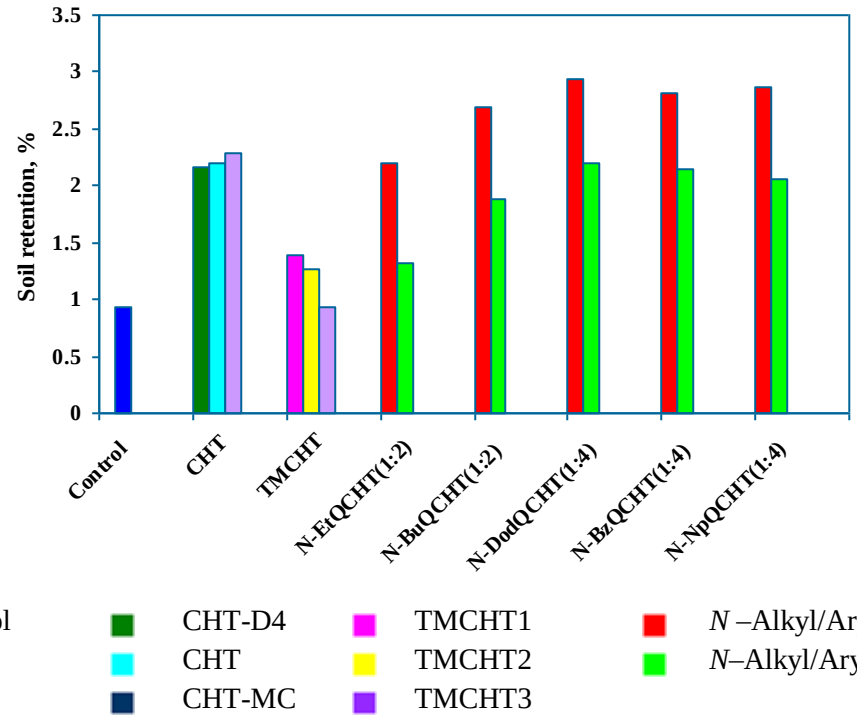
Sample	***N*-Alkyl/Aryl CHT treated fabric**			**Sample**	***N*-Alkyl/Aryl Q CHT treated fabric**		
	Initial wt (A), g	**Wt after soaping (B), g**	**Soil retention, %** $\frac{B-A}{A}\times 100$		**Initial wt (A), g**	**Wt after soaping (B), g**	**Soil retention, %** $\frac{B-A}{A}\times 100$
Control	1.2949	1.3071	0.94	Control	1.2949	1.3071	0.94
CHT-D4	1.2653	1.2928	2.17	TMCHT 1	1.2553	1.2738	1.39
CHT	1.2611	1.2888	2.20	TMCHT 2	1.2388	1.2544	1.26
CHT-MC	1.3260	1.3562	2.28	TMCHT 3	1.2637	1.2756	0.94
N-Et CHT (1:2)	1.2932	1.3217	2.20	N-Et Q CHT(1:2)	1.2680	1.2847	1.32
N-Bu CHT (1:2)	1.2688	1.3029	2.69	N-Bu Q CHT (1:2)	1.2813	1.3054	1.88
N-Dod CHT (1:2)	1.2731	1.3101	2.93	N-Dod Q CHT(1:2)	1.2771	1.3050	2.19
N-Bz CHT (1:4)	1.2589	1.2943	2.81	N-Bz Q CHT (1:4)	1.2689	1.2962	2.15
N-Np CHT (1:4)	1.2813	1.3179	2.86	N-Np Q CHT (1:4)	1.2800	1.3066	2.05

Conc in pad bath 10 g/L, Mol wt: CHT-D4:20698, CHT: 135,839, CHT-MC: 654,127,
DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Thus, in order to evaluate the performance of *N*-substituted CHT derivatives for soil release properties, the CHT derivatives pretreated cotton fabrics were subjected to soiling with olive oil, a major component of human sebum, and vacuum cleaner dirt. Evaluations of S.R property performed both gravimetrically by determining percentage soil take up and soil retention; and optically in terms of degree of soiling [56, 57] and yellowness index (Y.I.) presented in Tables 4.38, 4.39 and 4.40 and graphically in Figures 4.40, 4.41 and 4.42.

Of the various analytical techniques employed for the evaluation of soiling tendency, the 'soil retention' characterized the actual amount of impurities (oil +

particulate soil) remained gravimetrically on the fibre. The differences among these values were very less. Hence only an apparent trend in the soiling behaviour was determined. Since small changes in soil retention can greatly alter the optical appearance both gravimetric and optical methods of evaluation were employed for the better understanding of soiling behaviour of CHT derivatives treated cotton fabric.



Conc in pad bath 10 g/L, Mol wt: CHT-D4:20698, CHT: 135,839, CHT-MC: 654,127, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.40 Effect of different chitosan and *N*- Sub CHT treatment on soiling of cotton fabric

Table 4.39 Effect of different CHT and *N*- sub CHT treatment on degree of soiling

Sample	*N*-Alkyl/Aryl CHT treated fabric			Sample	*N*-Alkyl/Aryl Q CHT treated fabric		
	$(K/S)_U$ Unsoiled	$(K/S)_S$ Soiled	Degree of Soiling $(K/S)_S$-$(K/S)_U$		$(K/S)_U$ Unsoiled	$(K/S)_S$ Soiled	Degree of Soiling $(K/S)_S$-$(K/S)_U$
Control	0.063	0.1852	0.122	Control	0.063	0.1852	0.122
CHT-D4	0.1464	0.4276	0.281	TMCHT 1	0.0937	0.2742	0.181
CHT	0.1476	0.4318	0.284	TMCHT 2	0.0846	0.2475	0.163
CHT-MC	0.1531	0.4478	0.295	TMCHT 3	0.0672	0.1943	0.127
N-Et CHT (1:2)	0.1479	0.4328	0.285	N-EtQ CHT(1:2)	0.0885	0.2589	0.170
N-Bu CHT (1:2)	0.1806	0.5184	0.348	N-Bu Q CHT (1:2)	0.1263	0.3696	0.243
N-Dod CHT (1:2)	0.1940	0.5676	0.374	N-Dod Q CHT(1:2)	0.1471	0.4303	0.283
N-Bz CHT (1:4)	0.1866	0.5459	0.354	N-Bz Q CHT (1:4)	0.1445	0.4228	0.278
N-Np CHT (1:4)	0.1905	0.5573	0.367	N-Np Q CHT (1:4)	0.1398	0.4091	0.269

Conc in pad bath 10 g/L, Mol wt: CHT-D4:20698, CHT: 135,839, CHT-MC: 654,127, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

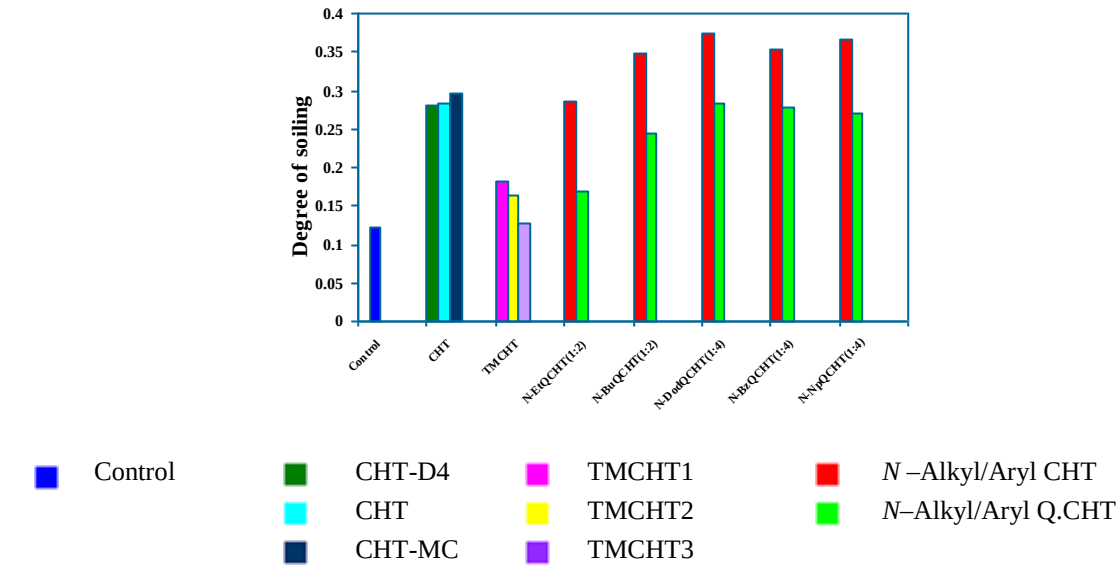


Figure 4.41 Effect of different CHT and *N*- sub CHT treatment on degree of soiling of cotton

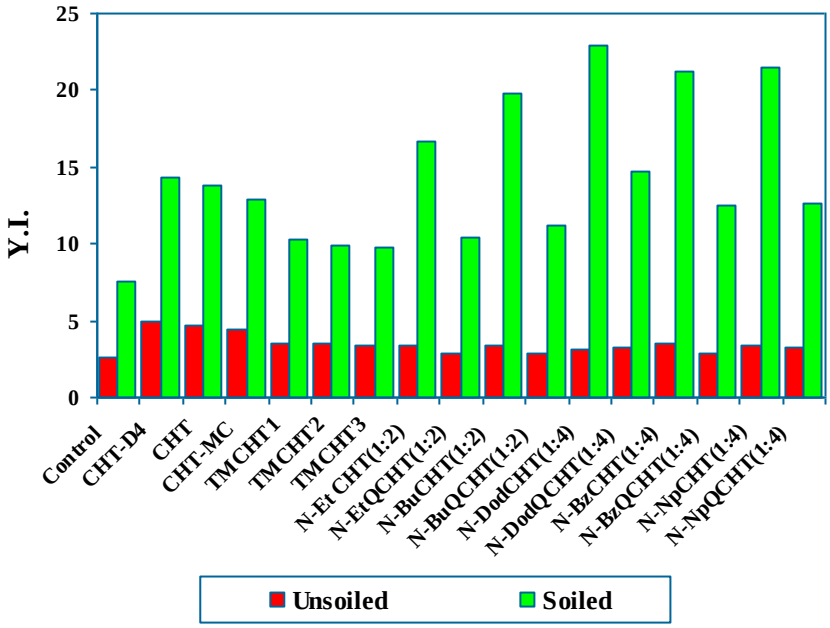
Table 4.40 Effect of different *N*- sub CHT treatment on yellowness index

Sample	*N*-Alkyl/Aryl CHT treated fabric			Sample	*N*-Alkyl/Aryl Q CHT treated fabric		
	DS, %	$YI_{(U)}$ Unsoiled	$YI_{(S)}$ Soiled		DS, %	$YI_{(U)}$ Unsoiled	$YI_{(S)}$ Soiled
Control	-	2.63	7.61	Control	-	2.63	7.61
CHT-D4	-	4.90	14.31	TMCHT 1	-	3.49	10.24
CHT	-	4.69	13.75	TMCHT 2	-	3.46	9.86
CHT-MC	-	4.4	12.87	TMCHT 3	-	3.35	9.83
N-Et CHT (1:2)	45.5	3.34	16.72	N-Et Q CHT(1:2)	45.5	2.85	10.48
N-Bu CHT (1:2)	40.1	3.34	19.83	N-Bu Q CHT (1:2)	40.1	2.84	11.19
N-Dod CHT (1:2)	37.6	3.07	22.91	N-Dod Q CHT(1:2)	37.6	3.26	14.65
N-Bz CHT (1:4)	44.9	3.48	21.23	N-Bz Q CHT (1:4)	44.9	2.88	12.49
N-Np CHT (1:4)	37.6	3.37	21.52	N-Np Q CHT (1:4)	37.6	3.28	12.66

Conc in pad bath 10 g/L, Mol wt: CHT-D4:20,698; CHT: 135,839; CHT-MC: 654,127; DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

It was observed from these results that the chitosan treated samples were soiled greatly than the control one. The molecular weight of chitosan could show little influence of the soil retention, which was increased slightly accordingly. The optical method parameters such as degree of soiling and yellowness index were, however, maximum for low molecular weight chitosan i.e. CHT-D4. This anomaly may be attributed to the comparatively higher yellowness of CHT-D4 acquired during depolymerization of CHT. It was further observed from these results that the soiling tendency of CHT derivative treated samples was increased with increase in chain length or molecular size due to *N*-alkyl or *N*-aryl substituents on chitosan. The quaternization of CHT and these *N*-substituted CHT derivatives was found to improve the soil release properties. The most pronounced effect was noticed with trimethyl chitosan derivative treated cotton fabrics. The soil repellency or release property was progressively improved with increase in its degree of quaternization. Also the soiling effect produced by *N*-alkyl or *N*-aryl groups

was substantially overcome by the quaternization although the effect of molecular size of substituents was sustained.



Conc in pad bath 10 g/L, Mol wt: CHT-D4:20698; CHT: 135,839; CHT-MC: 654,127; DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.42 Effect of quaternized *N*- sub CHT treatment on yellowness index

The soiling tendency of chitosan may be attributed to its two inherent properties namely the cationic nature and the lipid binding. Soil particulates being negatively charged often get attracted towards positively charged surfaces. It has been well documented that the chitosan macromolecules bind lipids to great extent [80-82]. The interaction between chitosan and oil is not clearly known but it is believed that the nucleophilic amino groups of chitosan can interact with electrophilic carbonyl carbon of ester bridges in oils. The carbonyl carbons being weakly electrophile due to adjacent electron releasing hydrocarbon chains, only weak forces of attraction between oil and amino groups of chitosan is established. Other forces H- bonding between carbonyl oxygen on oils and hydrogen of amino groups on chitosan; and obviously Van der Waal's forces may also contribute to the attachment of lipids onto chitosan.

When the hydrophobicity of chitosan was increased, as observed from Table 4.30, by increasing the hydrocarbon chain length in alkyl group or by increasing the aromatic

rings or hydrocarbon chain in aryl substituents, the possibility of polarization forces are reduced due to these bulkier side groups and the hydrophobic -hydrophobic interaction between *N*-alkyl or *N*-aryl and the hydrocarbon chains of oils is established. These interactions are very much similar to the partial dissolution of hydrocarbon chain of oils into hydrophobic groups of *N*-substituent on chitosan and vise versa due to similar forces of attraction between them quantified by a terminology solubility parameter (δ) [83] and lead to fat binding. Quaternization of chitosan and *N*-substituted chitosan derivatives converts the primary and secondary amines into permanent cations. These ions, due to ion dipole forces, interact with surrounding water molecules in the washing bath and get hydrated. The improved absorbency of cotton fabric treated with quaternized CHT and *N*-substituted CHT derivatives can be seen from the Table 4.30. This improved hydrophilicity facilitates the removal of soil as explained by Erik Kissa's mechanism [84]. According to this, the particulate soil is removed from fibres by a two step process. First, a thin layer of wash liquor penetrates between the particle and the fibre surface, enabling surfactants to adsorb onto particle surface as shown in Figure 4.43. Then, the particle becomes solvated and is transported away from the fibre and into the bulk of the wash liquid by mechanical action. Thus the modification of chitosan by *N*-alkyl or *N*-aryl substitution for the enhanced/improved handle and antibacterial was needed to be compromised with poor soil release property. The quaternization of these derivatives improved the hydrophilicity of treated fabric and also the soil release properties, yet the discrepancy due to hydrophobic substituents still persist. An extensive research in this domain is in demand.

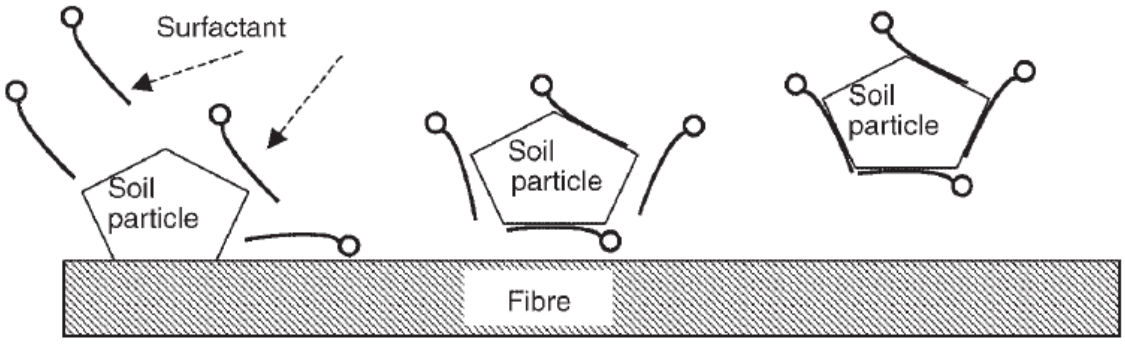


Figure 4.43 Release of particulate soil from fibre surface

4.3.3.10 Effect of N- substituted CHT treatment on resistance against microorganism of cotton fabric

As discussed in previous chapters, chitosan was found to exhibit antibacterial activity and was improved when scaled down to nano level and in conjunction with nano silver. The CHT, however, has poor solubility at neutral and therefore is almost inactive or weakly active [27]. In fact, the objective of the chitosan derivatives synthesis was to enhance such intrinsic property of chitosan. Thus the effect of quaternization and *N*- alkyl and *N*-aryl substituents of varying molecular size (hydrophobicity) on resistance to microbial attack on cotton fabric substrate was evaluated through soil burial test.

Table 4.41A Effect of different *N*- Alkyl/Aryl CHT treatment on resistance against microbial attack of cotton fabric (soil burial test)

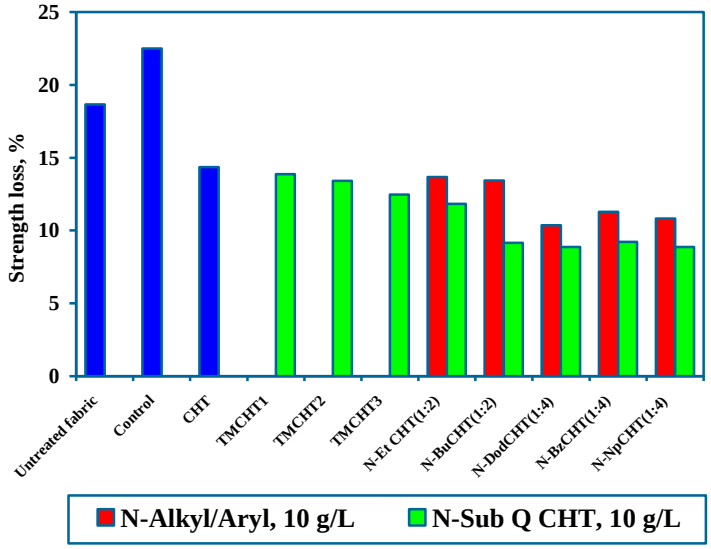
Sample	DS, %	Tenacity, g/tex		Strength loss, %	Elongation at break, %	
		Before soil burial	After soil burial		Before soil burial	After soil burial
Untreated cotton fabric	-	23.33	18.98	18.65	5.25	3.50
Control	-	20.87	18.08	22.50	5.00	3.50
CHT	-	21.77	18.64	14.36	4.50	3.75
N-Et CHT (1:2)	45.5	21.96	18.96	13.67	5.00	4.00
N-Bu CHT (1:2)	40.1	21.08	18.25	13.44	4.75	4.50
N-Dod CHT(1:4)	37.6	21.88	19.61	10.36	5.25	4.50
N-Bz: CHT (1:4)	44.9	22.01	19.53	11.29	5.00	5.00
N-Np: CHT (1:4)	37.6	20.53	18.31	10.83	5.00	4.75

Conc in pad bath 10 g/L

Table 4.41B Effect of different *N*- Alkyl/Aryl Q CHT treatment on resistance against microbial attack of cotton fabric (soil burial test)

Sample	DQ, %	Tenacity gm/tex		Strength loss, %	Elongation, %	
		Before soil burial	After soil burial		Before soil burial	Before soil burial
Untreated cotton fabric	-	23.33	18.98	18.65	5.25	3.50
Control	-	20.87	18.08	22.50	5.00	3.50
CHT	-	21.77	18.64	14.36	4.50	3.75
TMCHT1	13.4	21.38	18.41	13.88	4.75	4.00
TMCHT2	22	21.81	18.88	13.42	5.00	4.00
TMCHT3	50.9	21.18	18.54	12.47	4.50	4.00
N-Et QCHT (1:2)	52	21.68	19.12	11.83	4.50	4.00
N-BuQCHT (1:2)	47.5	20.14	18.30	9.16	5.25	4.00
N-DodQCHT(1:4)	45.1	21.36	19.47	8.87	5.00	3.75
N-Bz QCHT (1:4)	41.4	21.81	19.80	9.22	4.75	4.00
N-NpQCHT (1:4)	40	19.92	18.19	8.86	5.25	4.00

Conc in pad bath 10 g/L



DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40

Figure 4.44 Effect different *N*- sub CHT treatments on resistance against microbial attack of cotton fabric (soil burial test)

It was observed from Tables 4.41 (A &B) and Figure 4.44 that with increase in degree of quaternization the resistance to microbial attack increased. The results revealed that the long chain alkyl group i.e. dodecyl chain and aromatic substituents were more effective than the CHT and quaternary ammonium CHT derivatives for almost same level of DS. When these *N*-substituted CHT derivatives were quaternized, the resistance to microbial attack enhanced. Microbial attack of cellulolytic microflora in a composted soil bed is considered to be the most rigorous and extremely varying depending upon the presence of type of microbes present and the conditions [85]. The action of quaternary ammonium group and the alkyl substituents of CHT on bacteria is associated with the interaction with their cell wall of bacteria [23, 27, 58]. The cell wall is a complex structure and for most of the microbes it is composed of lipopolysaccharide and/or peptidoglycan both having an ionic groups due to phosphates, carboxylates, *N*-acetylmuramic acid etc that can interact with poly cations of CHT derivatives due to quaternary salts. The chelent effect of quaternary salts on divalent cations present on cell wall also contributes to disrupt the integrity of the membrane. In fact, the better antibacterial of quaternary salts cannot rely only on charge density because at acid medium the CHT chain is almost protonated. It is also necessary to consider the degree of ionization and the chain conformation [46]. The chain conformation of quaternized CHT is flexible due to comparatively weaker repulsive forces among quaternary groups than CHT amino groups, which facilitates the interaction with bacteria cell envelope.

The antibacterial property imparted due to the introduction of large hydrophobic moiety on amine group of CHT may be ascribed to the hydrophobic affinity between alkyl chain and phospholipids of bacterial membrane [23, 27, 43, 44, 58]. The phospholipids of bacterial cytoplasmic membrane, besides hydrophilic anionic groups, contain long chain hydrophobic ends of fatty acid tails with carbon number of 12 to 20. Thus, the cationic charge due to quaternized group, hydrophobicity and flexible conformation were found to be important factors in enhancing the antibacterial activity.

The encouraging results of *N*-substitution and quaternization of CHT for antimicrobial activity on undyed cotton fabric inspired to extend the work on dyed fabrics. The performance of quaternized and *N*- substituted quaternized CHT derivatives

on dyed cotton fabric for antimicrobial property is presented in Tables 4.42 (A&B) and Figures 4.45 and 4.46.

It was observed from these results that the undyed and dyed blank treated cotton fabrics degraded to maximum extent due to microbial attack. The strength losses were somewhat higher side in dyed fabrics. The influence of post dyeing treatment of *N*- alkyl and *N*-aryl CHT derivatives on microbial attack were found to be nominal where as the post dyeing treatment of CHT and quaternized CHT derivatives showed somewhat deprecation to microbial resistance. The strength losses due to dyeing were more prominent in TMCHT and N-Et Q CHT treated fabric, particularly, on blue dyed fabrics.

Table 4.42A Effect of different *N*- Alkyl/Aryl CHT treatment on resistance against microbial attack of dyed cotton fabric (soil burial test)

Sample	DS, %	C.I. Direct Blue 71			C. I. Direct Red 81		
		Tenacity, g/tex		Strength loss, %	Tenacity, g/tex		Strength loss, %
		Before soil burial	After soil burial		Before soil burial	After soil burial	
Untreated dyed fabric	-	22.68	18.32	19.33	22.73	18.42	18.96
Control (Dyed- blank treated)	-	20.66	15.89	23.08	20.81	16.14	22.43
CHT	-	21.59	18.06	16.33	21.14	17.95	17.04
N-Et CHT (1:2)	45.54	21.87	19.02	12.81	21.69	18.84	13.16
N-Bu CHT (1:2)	40.13	22.11	19.19	13.22	21.35	18.61	13.62
N-Dod CHT(1:4)	37.63	21.64	19.33	10.88	22.23	19.27	11.29
N-Bz CHT (1:4)	44.89	21.89	19.50	10.92	20.96	18.59	11.33
N-Np CHT (1:4)	37.57	22.11	19.84	10.26	21.29	19.08	10.38

Dye 1% o.w.m, Conc of CHT derivatives in pad liquor 10g/L

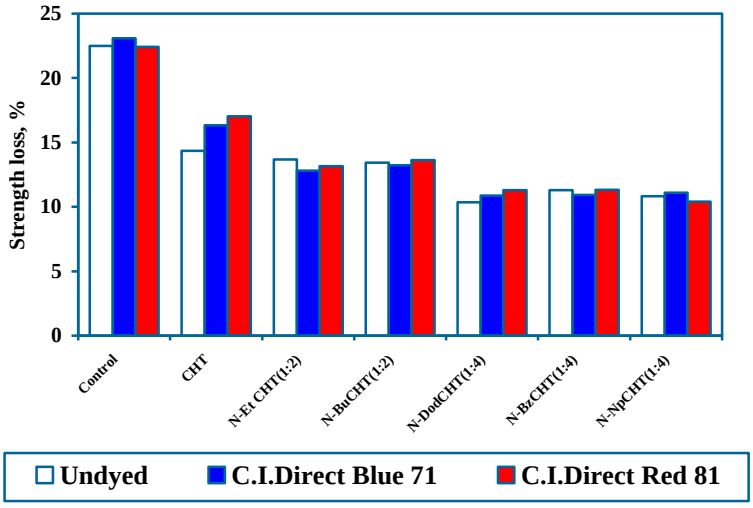
Table 4.42B Effect of different *N*- Alkyl/Aryl QCHT treatment on resistance against microbial attack of dyed cotton fabric (soil burial test)

Sample	DQ, %	C. I. Direct Blue 71			C.I. Direct Red 81		
		Tenacity, g/tex		Strength loss, %	Tenacity, g/tex		Strength loss, %
		Before soil burial	After soil burial		Before soil burial	After soil burial	
Untreated dyed fabric	-	22.68	18.32	19.33	22.73	18.42	18.96
Control (Dyed- blank treated)	-	20.66	15.89	23.08	20.81	16.14	22.43
CHT	-	21.59	18.06	16.33	21.14	17.95	17.04
TMCHT1	13.41	21.35	18.28	14.38	21.12	18.02	14.68
TMCHT2	22.43	21.66	18.60	14.12	21.33	18.38	13.85
TMCHT3	50.92	20.88	18.03	13.64	21.08	18.25	13.42
N-Et QCHT (1:2)	51.72	22.19	19.19	12.52	21.64	18.94	12.47
N-Bu QCHT (1:2)	47.46	21.49	19.01	11.56	21.96	19.68	10.37
N-Dod QCHT(1:4)	45.00	20.93	19.14	08.56	21.48	19.41	9.63
N-BzQCHT (1:4)	41.44	21.72	19.57	10.11	22.18	19.65	11.39
N-NpQCHT (1:4)	39.96	22.06	19.92	9.69	21.89	19.62	10.36

Dye 1% o.w.m, Conc of CHT derivatives in pad liquor 10g/L

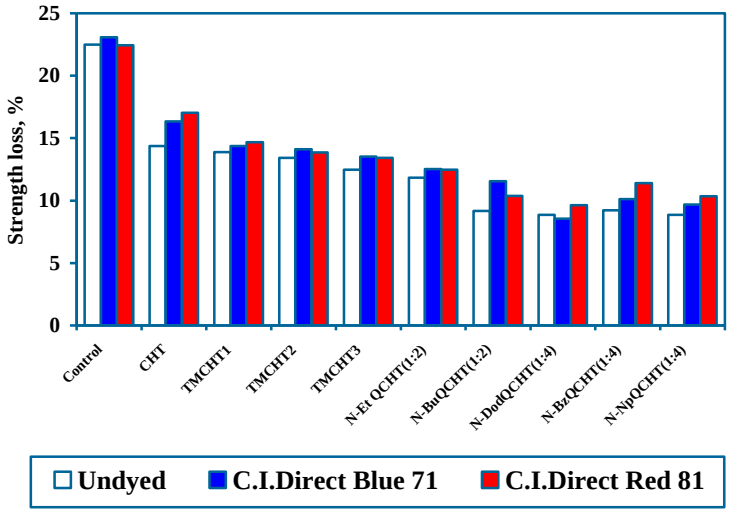
The detrimental effect of dyed fabrics to microbial resistance of quaternized CHT derivatives may be attributed to the neutralization of positive charges with anionic sulphonate groups on direct dyes. Presence of more number of $-SO_3^-$ groups in C. I. Direct Blue 71 than that of red dye, as observed from chemical structures shown in Table 4.1, may be the decline in effectiveness of blue dyed fabric to the microbial resistance. The antibacterial property *N*- sub Q CHT derivatives on dyed fabrics was yet sustained, Figures 4.45 and 4.46, due to *N*- alkyl or *N*-aryl substituents and also to the presence of

excessively large number of cations on Q CHT derivative molecules than the sulphonate anions on dye molecule.



Dye 1 % o.w.m, Conc in pad bath 10 g/L, DS(%): N-Et CHT=45.5, N- Bu CHT (1:2) = 40.1, N-Dod CHT (1:4)= 37.6, N-Bz CHT (1:4)= 44.9, N-Np CHT(1:4)= 37.6

Figure 4.45 Effect different *N*- Alky//Aryl CHT treatments on resistance against microbial attack of dyed cotton fabric (soil burial test)



Dye 1 % o.w.m, Conc in pad bath 10 g/L, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; N-Et QCHT=52, N- Bu Q CHT (1:2) = 47.5, N-Dod Q CHT (1:4)= 45.1, N-Bz Q CHT (1:4)= 41.4, N-Np Q CHT(1:4)= 40

Figure 4.46 Effect different quaternized *N*- sub CHT treatment on resistance against microbial attack of dyed cotton fabric (soil burial test)

REFERENCES

1. Dierk Knittel, Gisela Materne and Eckhard Schollmeyer, "Degradation of chitosan sizes", *Melliand English*, **87**(9) Sept (2006) E 142-E144.
2. V.A. Shenai and N.M. Saraf, *Tech of Finishing*, Vol X, 5th edition Sevak Publishers, Mumbai (1987)
3. J.T. Marsh, *An Introduction to Textile Finishing*, Sixth (revised) Impression Asia Publishing House, Mumbai (1957)
4. C. S. Chen, J. C. Su, G. J. Tsai, *Advances in Chitin Science*; Vol. III, R.H. Chen and H.C. Chen (Eds), Rita Advertising Co. Ltd., Taiwan, (1998)278-282
5. Fatih Karadeniz, Mustafa Zafer Karagozlu, Sang-Yong Pyun, Se-Kwon Kim, "Sulfation of chitosan oligomers enhances their anti-adipogenic effect in 3T3-L1 adipocytes", *Carbohydrate Polymers* **86** (2) (2011)666–671
6. Po Liang, Ying Zhao, Qiang Shen, Dujin Wang, Duanfu Xu, "The effect of carboxymethyl chitosan on the precipitation of calcium carbonate", *Journal of Crystal Growth*, **261,** (2004) 571–576
7. A. Pourjavadi and G.R. Mahdavinia, "Superabsorbancy, P^H sensitivity and swelling kinetics of partially hydrolyzed chitosan-g-polyacrylamide hydrogels", *Turkish Journal of Chemistry,* **30** (2006) 595-608
8. Trang-Ming Don, Chung-Yan Chuang and Wen-Yen Chiu; "Studies on the degradation behaviour of chitosan-g-poly (acrylic acid) copolymers", *Tamkang Journal of Science & Engineering,* **5** (4) (2002) 235-240
9. T. T. Nge, N. Hori, A. Takemura, H. Ono, "Swelling behaviour of chitosan/ polyacrylic acid complex", *Journal of Applied Polymer Science.* **92**(5) (2004) 2930-2940
10. Tatjama Romaskevic, Saulute Budriene, Aurelija Liubertiene, Irina Gerasimick, Asta Zubriene and Gervydas Dienys, "Synthesis of chitosan-g-poly (Ethylene Glycol) methyl ether methacrylate copolymer and its application for immobilization of maltogenase", *CHEMIJA,* **18** (2) (2007) 33-38
11. S. Hirano, "Chitin and Chitosan", *Ullmann's Encyclopaedia of Ind. Chemistry,* Vol. 7, Ed no 6 Wiley-VCH, Weinheim (Germany) (2003) 679-691

12. Chun Ho Kim and Kyu Suk Choi, "Synthesis and Properties of carboxyalkyl Chitosan Derivatives", *Journal of Industrial and Engineering Chemistry,* **4**(1) (1998) ***19***-25
13. J. Desbrieres, C. Martinez, M. Rinaudo, "Hydrophobic derivatives of chitosan: characterization and rheological behaviour" *International Journal of Biological Macromolecules*, **19**(1) (1996) 21-29
14. W.H. Daly and M.M. Guerrini, "Antimicrobial properties of quaternary ammonium cellulose and chitosan derivatives", *Polymeric Materials Science and Engineering*, **79** (1998) 220-221
15. Kim, C.-H.; Kim, S.-Y.; Choi, K.-S., "Antibacterial activity of water soluble chitin derivatives", *Polym. Advan. Technol.* **8**(5) (1997) 319-325
16. A. Bayat, A.M.M. Sadeghi, M.R. Avadi, M. Amini, M. Rafiee- Tehrani, A. Shafiee, H.E. Junginger "Synthesis of N, N-dimethyl N-ethyl Chitosan as a Carrier for Oral Delivery of Peptide Drugs", *Journal of Bioactive and Compatible Polymers*, **21**, (2006) 433-444
17. A. Domard, M. Rinaudo and C. Terrassin, "New method for the quaternization of chitosan," *International Journal of Biological Macromolecules*, **8**(2) (1986)105–107
18. Wei Liang XU, Jun WU, Chun Ling FU, Synthesis of Chitosan Quaternary Ammonium Salts, *Chinese Chemical Letters*, **12** (12) (2001) 1081 –1084
19. D. Snyman, J.H. Hamman, J.S.Kotze, J.E.Rollings, A.F. Kotze, "The relationship between the absolute molecular weight and the degree of quaternization of N-trimethyl chitosan chloride", *Carbohydrate Polymers*, **50** (2002) 145-150
20. A.B. Sieval, M. Thanoual, A.F. Kotzk, J.C. Verhoef, J. Brussee, H.E. Junginger, "Preparation and NMR characterization of highly substituted IV trimethyl chitosan chloride", *Carbohydrate Polymers*, **36** (1998) 157-165
21. W.B.Achwal, "Use of chitin and its derivatives in textile processing", *Colourage*, **XLVII** (9) September (2000) 47-48
22. B. S. Bahl and Arun Tuli, *Advanced Organic Chemistry*, 2nd edition, S. Chand and Co Ltd., N.Delhi (1983)

23. Chun Ho Kim and Kyu Choi, "Synthesis and antibacterial activity of quaternized derivatives having different methylene spacers", *Journal of Industrial and Engineering Chemistry*, **8** (1) (2002) 71-76
24. Entsar I Rabea, Mohamed EI Badawy, Tina M Rogge,Christian V Stevens,Monica Hofte,Walter Steurbaut and Guy Smagghe, "Insecticidal and fungicidal activity of new synthesized chitosan derivatives", *Pest Management Science,* **61** (2005) 951–960
25. Entsar I Rabea, Mohamed EI Badawy, Tina M Rogge, Christian V Stevens, Walter Steurbaut, Monica Hofte and Guy Smagghe, "Enhancement of fungicidal and insecticidal activity by reductive alkylation of chitosan", *Pest Management Science,* **62** (2006) 890–897
26. Nadhratun Naiim Mobarak, Md.Pauzi Abdullah, "Synthesis and characterization of several lauryl chitosan derivatives", *The Malaysian Journal of Analytical Sciences*, **14 (**2) (2010) 82 – 99
27. Warayuth Sajomsang, Supawan Tantayanon, Varawut Tangpasuthadol, William H. Daly, "Quaternization of N-aryl chitosan derivatives: synthesis, characterization, and antibacterial activity", *Carbohydrate Research*, **344** (2009) 2502–2511
28. Elena Bobu, Raluca Nicu, M. Lupei, Fl. Ciolacu And J. Desbrières, "Synthesis and characterization of n-alkyl chitosan for papermaking applications", *Cellulose Chem. Technol*., **45** (9-10), (2011) 619-625
29. R. A. A. Muzzarelli and F. Tanfani, "The *N*-permethylation of chitosan and the preparation of *N*-trimethyl chitosan iodide", *Carbohydrate Polymers*, **5**(4) (1985) 297–307
30. D. de Britto and O. B. G. Assis, "A novelmethod for obtaining a quaternary salt of chitosan," *Carbohydrate Polymers*, **69** (2) (2007)305–310
31. Elisabete Curtia, Sergio Paulo Campana-Filho, "Viscosity Behavior of Chitosan and N,N,N-Trimethylchitosan Chloride Salts in Acid-Free Aqueous Solution" *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, **43** (2006) 555–572
32. Douglas de Britto, Sérgio P. Campana-Filhon, Odilio B.G. de Assis, "Mechanical

Properties of *N,N,N*-trimethylchitosan Chloride Films", *Polímeros: Ciencia e Tecnologia*, **15** (2) (2005) 142-145

33. D. de Britto and S. P. Campana-Filho, "A kinetic study on the thermal degradation of *N,N,N*-trimethylchitosan", *Polymer Degradation and Stability*, **84** (2) (2004) 353–361
34. J. Murata, Y. Ohya, and T. Ouchi, "Possibility of application of quaternary chitosan having pendant galactose residues as gene delivery tool," *Carbohydrate Polymers*, **29**(1) (1996)69–74
35. J. Murata, Y. Ohya, and T. Ouchi, "Design of quaternary chitosan conjugate having antennary galactose residues as a gene delivery tool," *Carbohydrate Polymers*, **32** (2) (1997)105–109
36. T. Kean, S. Roth, and M. Thanou, "Trimethylated chitosans as non viral gene delivery vectors: cytotoxicity and transfection efficiency," *Journal of Controlled Release*, **103** (3) (2005) 643–653
37. M.M. Thanoua, A.F. Kotze´, T. Scharringhausena, H.L. LueBen, A.G. de Boerd, J.C. Verhoefa, H.E. Junginger, "Effect of degree of quaternization of *N*-trimethyl chitosan chloride for enhanced transport of hydrophilic compounds across intestinal Caco-2 cell monolayers", *Journal of Controlled Release* , **64** (1-3) (2000) 15–25
38. M.Werle, H. Takeuchi, and A. Bernkop-Schnurch, "Modified chitosans for oral drug delivery," *Journal of Pharmaceutical Sciences*, **98** (5), (2009)1643–1656
39. V. K. Mourya and N. N. Inamdar, "Trimethyl chitosan and its applications in drug delivery," *Journal of Materials Science*, **20** (5) (2009)1057–1079
40. J. K. Sahni, S. Chopra, F. J. Ahmad, and R. K. Khar, "Potential prospects of chitosan derivative trimethyl chitosan chloride (TMC) as a polymeric absorption enhancer: synthesis, characterization and applications," *Journal of Pharmacy and Pharmacology*, **60** (9) (2008)1111–1119
41. A. F. Kotze, H. L. LueBen, B. J. de Leeuw, B. G. de Boer, J. C. Verhoef, andH. E. Junginger, "*N*-Trimethyl chitosan chloride as a potential absorption enhancer across mucosal surfaces: *in vitro* evaluation in intestinal epithelial cells (Caco-2)," *Pharmaceutical Research*, **14** (9) (1997)1197–1202

42. R.Tanaka, J. Meadows, G.O.Phillips and P.A.Williams, "Viscometric and spectroscopic studies on the solution behavior of hydrophobically modified cellulosic polymers" *Carbohydrate Polymers.* **12** (1990) 443 -459
43. C. H. Kim, J.W. Choi, H. J. Chun, and K. S. Choi, "Synthesis of chitosan derivatives with quaternary ammonium salt and their antibacterial activity," *Polymer Bulletin*, **38**,(4) (1997)387–393
44. Z. Jia, D. Shen, and W. Xu, "Synthesis and antibacterial activities of quaternary ammonium salt of chitosan", *Carbohydrate Research*, **333** (1) (2001)1–6
45. W. Sajomsang, S. Tantayanon, V. Tangpasuthadol, andW. H. Daly, "Synthesis of methylated chitosan containing aromatic moieties: chemoselectivity and effect on molecular weight", *Carbohydrate Polymers*, **72 (**4) (2008)740–750
46. T. Xu, M. Xin, M. Li, H. Huang, and S. Zhou, "Synthesis, characteristic and antibacterial activity of *N,N,N*-trimethyl chitosan and its carboxymethyl derivatives", *Carbohydrate Polymers*, **81**(4) (2010) 931–936
47. A.M.M. Sadeghi, M. Amini, M.R. Avadi, F. Siedi, M. Rafiee Tehrani, H.E. Junginger, Chapter 2, "Synthesis, characterization and antibacterial effects of trimethylated and triethylated 6-NH2-6-Deoxy Chitosan", *Journal of Bioactive and Compatible Polymers*, **23,** (2008) 262-275
48. D. de Britto, L. A. Forato, and O. B. G. Assis, "Determination of the average degree of quaternization of *N,N,N*trimethylchitosan by solid state 13C NMR," *Carbohydrate Polymers*, **74** (1) (2008) 86–91
49. O. V. R´unarsson, J. Holappa, S. J´onsd´ottir, H. Steinsson and M. M´asson, "N-selective 'one pot' synthesis of highly N- substituted trimethyl chitosan (TMC)," *Carbohydrate Polymers*, **74** (3), (2008)740–744
50. Worawan Boonyo, Hans E. Junginger, Neti Waranuch, Assadang Polnok And Tasana Pitaksuteepong, "Preparation and Characterization of Particles from Chitosan with Different Molecular Weights and Their Trimethyl Chitosan Derivatives for Nasal Immunization", *Journal of Metals, Materials and Minerals*, **18** (2)(2008)59-65
51. B. Slutter, L. Plapied, V. Fievez et al., "Mechanistic study of the adjuvant effect of biodegradable nanoparticles in mucosal vaccination," *Journal of Controlled*

Release, **138** (2), (2009)113–121

52. A. M. M. Sadeghi, F. A. Dorkoosh, M. R. Avadi, P. Saadat, M. Rafiee-Tehrani, and H. E. Junginger, "Preparation, characterization and antibacterial activities of chitosan, *N*-trimethyl chitosan (TMC) and *N*-diethylmethyl chitosan (DEMC) nanoparticles loaded with insulin using both the ionotropic gelation and polyelectrolyte complexation methods," *International Journal of Pharmaceutics*, **355** (1-2) (2008) 299–306
53. Kim, Y.H., Choi, H.M. and Yoon, J.H., "Synthesis of quaternary ammonium derivatives of chitosan and its application to a cotton antimicrobial finish" *Textile Research Journal,* **68**(6) June (1998) 428-434
54. Sang–Hoon Lim and Samuel Hudson, "Application of fibre-reactive chitosan derivative to cotton fabric as a zero salt dyeing auxiliary" *Coloration Technology,* **120** (2004) 108-113
55. N. Sekar, "Chitosan in textile processing-an update." *Colourage*; **XLVII** (7) July (2000) 33-34
56. AATCC Test Method 151-1990, AATCC Technical manual 1997, "Soil Redeposition, Resistance to: Launder-o-meter", Pg 260
57. M. Yatagai and Y. Takahashi, "Effect of citric acid DP finishing on soiling with particulate soil of cotton fabric" *AATCC Review,* **5**(1) Jan.(2005) 17-21
58. Douglas de Britto, Rejane Celi Goy, Sergio Paulo Campana Filho, and Odilio B. G. Assis, "Quaternary Salts of Chitosan: History, Antimicrobial Features, and Prospects", *International Journal of Carbohydrate Chemistry,* **2011**, (2011) 1-12
59. Ping Li, Ya-Ni Dai, Jun-Ping Zhang, Ai-Qin Wang , Qin Wei, "Chitosan–Alginate Nanoparticles as a Novel Drug Delivery System for Nifedipine", *International Journal of Biomedical science,* **4**(3) (2008) 221-228
60. Guanghua Liu, Jianqun Gan, Aimin Chen, Qian Liu, Xusheng Zhao, "Synthesis and characterization of an amphiphilic chitosan bearing octyl and methoxy polyethylene glycol groups", *Natural Science,* **2(**7) (2010) 707-712
61. J. H. Hamman and A. F. Kotze, "Effect of the type of base and number of reaction steps on the degree of quaternization and molecular weight of *N*-trimethyl chitosan chloride," *Drug Development and Industrial Pharmacy,* **27** (5),

(2001)373– 380

62. A. F. Kotze, H. L. Lueßen, B. J. de Leeuw, B. G. de Boer, J. C. Verhoef, and H. E. Junginger, "Chitosans for enhanced delivery of therapeutic peptides across intestinal epithelia: *in vitro* evaluation in Caco-2 cell monolayers," *International Journal of Biological Macromolecules*, **159**(20) (1997) 243–253
63 E. A. Stepnova, V. E. Tikhonov, T. A.Babushkina, T. P. Klimova, E. V. Vorontsov, V.G. Babak, S. A. Lopatin and I. A. Yamskov, "New approach to the quaternization of chitosan and its amphiphilic derivatives" *European Polymer Journal*; **43**, (2007) 2414
64. W. Sui, Y. Wang, S. Dong and Y. Chen, "Preparation and properties of an amphiphilic derivative of succinyl-chitosan", *Colloid*s and *Surface A***:** *Physicochemical and Engineering Aspects*; **316**, (2008) 171-175
65. G. Ma, D. Yang, J. F. Kennedy and J. Nie, "Synthesize and characterization of organic-soluble acylated chitosan", *Carbohydrate Polymerization*; **75**, (2009) 390-394
66. P.S.Kalsi, "Chapter.3, Infrared Spectroscopy", *Spectroscopy of Organic Compounds*, 6th Edition, New Age International Publisher, N. Dehli, India (2004) 59-164
67. Cristóbal Lárez Velásquez, Joel Sánchez Albornoz & Enrique Millán Barrios, "Viscometric stidies of chitosan nitrate and chitosan chlorhydrate in acid free NaCl aq solution", *e-Polymers*, No.014 (2008)1-8
68. J. Z. Knaul, V. T. Bui, K. A. M. Creber, and M. R. Kasaai, "Characterization of deacetylated chitosan and chitosan molecular weight review," *Canadian Journal of Chemistry*, **76** (11) (1998) 1699–1706
69. V. R. Gowariker, N. V. Viswanathan, and Y. Sreedhar, "Polymer solutions," *Polymer Science*, New Age International, New Delhi, India, (1986) 332–362
70. Jae Kwan Hwang and Hae Hun Shin, "Rheological properties of chitosan solutions", *Korea-Australia Rheology Journal*, **12** (3/4)**,** December (2000) 175-179
71. M. Terbojevich and R. A. A. Muzzarelli, "Chitosan", *Handbook of Hydrocolloids,* Phillips G O & Williams P A (Ed), Woodhead Publishing Ltd,

Cambridge, UK, (2000) 367- 378

72. Catherine Esquenet, Pierre Terech, Francüois Boue´ and Eric Buhler, "Structural and Rheological Properties of Hydrophobically Modified Polysaccharide Associative Networks"; *Langmuir,* **20**, (2004) 3583-92
73. W.D.Schindler and P.J.Hauser, "Chapter 7, Soil release Finishes", *Chemical finishing of textiles*, Woodhead publishing Ltd, Cambridge, England, (2004) 87-97
74. Charles H.Giles, "Dye-fibre bonds and their investigation", *The theory of coloration of textiles*, Alan Johnson(ed), 2nd edition, Society of dyers and colourists, West Yorkshire, England (1989) 97-168
75. V.A.Shenai, *Technology of Dyeing*, **VI**, 3rd edition, Sevak Publishers, Mumbai (1984)
76. Robert W. Harper, "The influence of grafted hydrophilic groups on the soil release characteristics of cross linked fabrics", *Textile chemists and colorists*, **17** (10) Oct (1985) 13-17
77. D.S.Williams and G.M.Greib, "Use of soil release finishes to promote attractivity of textiles based on polyester". *Melliand Textilberichte (Eng.Ed),* Feb.1983, 157-162
78. S.A.Weglinski and S.K.Obendorf, "Soil distribution on fabric after laundering", *Textile chemists and colorists,* **17** (10) Oct (1985) 21-24
79. Latta, B.M. and Sells, S.B. "Oily soil release for easy care cotton fabrics"; *Textile Research Journal*, **51**(9)Sept (1981) 579-587
80. O .Kanauchi, K. Deuchi,Y. Imasato, M. Shizukuishi and E. Kobayashi, "Increasing effect of a chitosan and ascorbic acid mixture on fecal dietary fat excretion", *Bioscience, Biotechnology and Biochemistry*, **58** (1994)1617-20
81. O .Kanauchi, K. Deuchi,Y. Imasato, M. Shizukuishi and E. Kobayashi, "Mechanism for the inhibition of fat digestion by chitosan and for the synergistic effect of ascorbate", *Bioscience, Biotechnology and Biochemistry*, **59**(5) (1995)786-90
82. M. Jumaa and B.W. Müller, "Physicochemical properties of chitosan-lipid emulsions and their stability during the autoclaving process", *International*

Journal of Pharmaceuticals, **183**(2) (1999) 175-84

83. H. Burrel and B. Immergut, "Solubilty parameter values" in Polymer handbook, J.Brandrup and E.H. Immergut (Edts), Interscience Publoshers, John Wiley & Sons, N.York (1966) IV/341- IV/368
84. Erik Kissa, "Mechanisms of soil release", *Textile Research Journal,* **51**(8) (1981) 508-513
85. E.L .Schmidt and O. R. Ruschmeyer, "Cellulose Decomposition in Soil Burial Beds: I. Soil Properties in Relation to Cellulose Degradation", *Applied Microbiology,* **6** (2) Mar (1958)108–114

CHAPTER 5
APPLICATION OF CHITOSAN AND ITS DERIVATIVES IN COMMERCIAL WATER PROCESSING AND EFFLUENT TREATMENT

5.1 INTRODUCTION

Plentiful supply of good quality water is indispensable for textile wet processing industry. Various unit operations of textiles such as sizing, desizing, scouring, bleaching, mercerizing, dyeing, printing and finishing etc consume and then discharge large quantity of water. Water is not only a vehicle to carry or fix the chemicals and dyes, but it is the medium for processing. It is an excellent wetting agent, and a best solvent for various dyes and chemicals. Textile processing related industries such as dyestuff manufacturing, chemicals & auxiliaries manufacturing etc are also of same concern. Other major applications of water include steam generation and cooling. Canteens and toilets also use considerable quantities. Besides, storage of large quantities of water is essential for fire fighting [1].

Textile wet processing operations produce high volumes of effluents waste water of varying composition. It contains various inorganic, organic and biological contaminants such as dyes, salts, alkali, mineral and organic acids, oils, solvents, surfactants, sequestering agents, oxidizing and reducing agents, polymers, silicones, formaldehyde based products and heavy metal ions etc that are of environmental significance contributing aquatic toxicity. It is, therefore, extremely essential that the environmental problems associated with industrial developments are properly addressed for sustainability. With the adoption of Water Act, all the industries including process houses have in theory the obligation to treat their effluent in order to reach pollution

---

Contents of this chapter is published in:
1) *Textile Research Journal, (In press),*
Accepted on: January 9, 2014, Manuscript ID TRJ-13-0412.R2
2) *International Journal of Polymer Science*, Vol 2010, (2010) 1-7

concentrations respecting the minimum acceptable standards laid down by the State Pollution Control Boards [2, 3].

Conventionally, the treatment of waste water is based on physico-chemical treatment followed by biological treatment. The waste water is collected in sump well and from where it is continuously taken up in to equalizing basin to neutralize quantitative irregularities. The waste water from equalization basin is treated with lime and ferrous sulphate for coagulation. The agglomerated flocculated material along with waste water enters into primary clarifier. The colloidal material along with some inorganics is removed here by sedimentation. The precipitated material comes out as sludge slurry and is finally dried up on sludge drying beds. The clarified liquid enters into activated sludge basin and is treated by acclimatized micro-organisms. The treated effluent from activated sludge basin is passed through a secondary clarifier to settle waste sludge. The sludge slurry is sent to sludge drying bed for disposal. The clear treated effluent from secondary clarifier passes through drain which finally disposes into the river [1, 2].

The discharged effluent after primary and secondary treatments, however, is extremely high with dissolved solids (3000 to 13000 ppm) containing Ca^{+2}, Mg^{+2}, Na^{+} and various heavy metal ions. In order to control the pollution load in streams (river, ground percolation or sea) it is best way to recycle the effluent back into processing operations. Here the effluent after conventional treatment is passed through the sand filters and carbon filters after disinfection by chlorine. The hardness of water is reduced in ion exchanger by passing it through polystyrene resin beds. After passing through ultra filtration plant, water is then taken through reverse osmosis (RO) plant which reduces the TDS [1, 4].

The water employed for various wet processing operations is now days largely obtained from underground source which is accompanied with various heavy metal ions. The recycled water from effluent discharge also contributes to these impurities due to the inefficiency of conventional ETPs to remove such traces of metal ions. The presence of these ions, even in ppm level, can have detrimental effects on processes like enzymatic desizing, hydrogen peroxide stability and its bleaching action, shade of dyes etc [5-7].

When these heavy metals and their compounds are discharged into streams like river, soil etc through industrial waste and sewage cause severe health and environmental problems.

Table 5.1 Characterization of river water and textile effluent

Metal ions	**Observed effluent composition, mg/L**		**Permissible limits for metal content(mg/L) in water used for:**		
			Textile processing	**Drinking**	
	***Textile effluent water [11]**	****Kasardi River [12]**	**The textile institute[1]**	**IS: 10500[13]**	**WHO[12]**
Arsenic (As)	-	-	-	0.05	-
Cadmium (Cd)	0.5	10.8 -21.3	-	0.01	0.01
Chromium (Cr^{+3}) (Cr^{+6})	1.5 (Cr^{+3})	14.7 -23.4	-	0.05	0.05
Copper (Cu)	3.62	31.9 -77	0.01	0.05	0.05 /0.10
Iron (Fe)	6.42	6.0 -8.8	0.3	0.3	0.30
Mercury (Hg)	-	-	-	0.001	-
Nickel (Ni)	0.4	5.6 -12.7	-	0.02	0.1
Lead (Pb)	0.37	19.7 -46.3	0.01	0.05	0.05
Total Hardness (as CaCO3)	-	-	70	300	-
Calcium (Ca)	1500	-	-	75	-
Magnesium (Mg)	-	-	-	30	-
Manganese (Mn)	5.4	-	0.05	0.1	-
Zinc (Zn)	1.0	8.3 -21.5	-	5	5.5

** Textile industry effluent collected from Coimbatore in Tamil Nadu, India, from Ref no 11,*
***Kasardi River is flowing along Taloja industrial area of Mumbai, India from Ref no 12*

Heavy metals ions like cadmium, chromium, nickel, arsenic and other hexavalent metal ions are carcinogenic. Lead can cause damage to human nervous system, impair IQ, brain

damage, kidney failure etc. Its acute lethal dose to human is 300-700 mg/kg. Mercury can cause brain damage and kidney failure or developing fetuses. Several disasters of metal poisoning have been recorded from time to time and led to a large number of human casualties [8-10]. The metal contamination discharged water and the permissible limit for such heavy metals in water used for drinking purpose and textile processing unit operations is given in Table 5.1. Removal of such heavy metal ions from supply water or effluent water has become prime requirement for green environment.

The adverse effect of these metal ions can be suppressed by following two techniques. One, by scavenging the metal ions with sequestering agents such as ethylene diamine tetra acetic acid (EDTA), diethylene triamine penta acetic acid (DTPA), nitrilo triacetic acid (NTA) etc or by precipitating /coagulating metal ions as salts alternatively reduced as metallic form. They can be separated from the liquid phase by filtration, settling, centrifuging or electro deposition [1, 10, 14]. Various natural products such as wood bark and clay [15], rice hull, cotton fibres, bamboo pulp, peanut skin etc and chitosan have been found to remove metal cations from the streams [16-19]. In the first method, the empty *d*-orbital of metal ions are supplied with electrons donated by organic ligands through coordinate linkages. The metal ions, in this method, are not actually removed from the bath but are inactivated. Such chelating agents can be incorporated in processing bath, e.g., in dyeing of textiles. Such bound metals, however, tend to exhaust onto fabric and/or discharge with the waste water [20]. The detrimental effects on environment of first route however still persist due to existence of metal ions in discharged water, while the metal ions are removed from discharged water by second route and therefore the is less hazardous to environment. As a sorbent in water processing a versatile biopolymer chitosan has gained wider attention due its high sorption capacity for metal ions and various classes of dyes such as disperse, direct, reactive, anionic, vat, sulphur and naphthols [21, 22]. Studies pertaining to efficient removal of dyes from textile effluent using chitosan is reported [3, 23, 24].

The application potential of chitosan and its derivatives for the recovery of valuable metals or the treatment of contaminated effluents is well reviewed by Alves and Mano [25] and Jaykumar et al. [26]. Mehdinejad et al. [27] examined the chitosan in conjunction with aluminum sulphate (alum) as coagulant on removal of turbidity and

bacteria from turbid water. They reported the turbidity removal efficiency of about 75-98% at pH range 7-7.5. In addition; chitosan significantly reduced the required doses of primary coagulant 50-87% and complete bacteria reduction within first 1-2 h treatment. The main effects of coagulation by chitosan on bacteria were enmeshment (entanglement) and stack on the microbial cell surface.

The mechanism by which metal ions are bound by chitosan probably involves attachment of these ions to $-NH_2$ groups. Because of these differences, it may be suitable for scavenging important heavy metal ions and complexes that cannot be adequately treated by other natural polymers [28, 29]. Guibal et el [30] suggested a surface control mechanism, indicating a monolayer sorption with interaction between the sorbed molecules and heterogeneous distribution of sorption energies. Karthikeyan et.al [31] studied the dynamics and equilibrium sorption of Zn (II) on to chitosan. They observed maximum of six minutes were required for complete sorption of Zn ions by chitosan obeying the Freundlich and Langmuir isotherms. The co-ions like Fe(III), Cu(II) and Cr(VI) were observed to inhibit the adsorption rate significantly. Nomanbhay and Palanisamy [32] used chitosan coated oil palm shell charcoal for the adsorption of chromium ions from water. They reported maximum adsorption of Cr ions on chitosan coated acid treated beads followed by chitosan coated beads. Bioconversion of highly toxic Cr(VI) into Cr(III) was also observed, which is essential in human nutrition especially in glucose metabolism. The recovery of precious metals such as silver, gold and platinum group metals is always attracting considerable attention due to the increasing industrial and domestic need and limiting sources. Chang and Chen [33] isolated/recovered Au (III) ions from water on monodisperse chitosan coated with Fe_3O_4 nanoparticles. They found that the gold ions could be fast and efficiently adsorbed, and the adsorption capacity increased with the decrease in pH due to the protonation of amino groups of chitosan. Adsorption data obeyed Langmuir isotherm.

In order to increase the density of sorption sites, to change the pH range for metal sorption and to change the sorption sites in order to increase sorption selectivity for the target metal new functional groups are incorporated into chitosan. Usually, the sorption behaviour of the derivatives follows the same the trend as raw chitosan. The grafting of carboxylic functions has frequently been regarded as an interesting process for increasing

the sorption properties of chitosan. Caboxymethyl chitosan have been prepared by reaction of chitosan with chloroacetic acid in propanol. Usually, the aim of these modifications is to design chelating derivatives for the sorption of metal cations [34-36]. Inoue et al have developed number of chitosan derivatives bearing carboxylic and amine groups by grafting EDTA by reaction of EDTA anhydride with chitosan [37]. The grafting of sulphur compounds on chitosan has been the subject of many studies for the design of chelating chitosan-based resins. These derivatives can be obtained by direct reaction of chitosan with carbon di sulphide to obtain dithiocarbamate chitosan [38]. These sulphur derivatives have been successfully tested for the recovery of mercury and the uptake of precious metals, owing to the chelating affinity of sulphur compounds for metal ions. Sulphonic groups have been also grafted on chitosan to improve sorption capacity for metal ions in acidic solutions [39]. Abdel Mohdy et al [40] introduced diethyl amino ethyl methacrylate (DEAEMA) groups onto chitosan backbone through radiation grafting and studied the chelation property of grafted derivative on copper, zinc and cobalt ions. They reported that the extent metal ions uptake by chitosan-DEAEMA derivative was preferentially higher for copper ions followed by zinc and cobalt ions.

Thus, attributing to the presence of large number of electrons donating amino and hydroxyl groups, chitosan exhibits metal ion binding property through co ordinate linkage. Further, with due respect to these functional groups, chitosan can lend itself to modify for the incorporation of tailor made functional groups for enhanced metal binding power. The present work was aimed at investigating the chelation property of chitosan and trimethyl chitosan chloride derivative. Chitosans of varying molecular weights were selected for this study. The chelation behaviour of nano chitosan dispersion obtained by gel ionization with pentasodium tripolyphosphate (TPP) was also investigated. The study was primarily performed on chelation of calcium ions (Ca^{++}) for its ease of analysis. The most popular volumetric evaluation method by titration with standard Na_2EDTA was employed for the Ca^{++} estimation. Study included the effect of molecular weight of chitosan, effect of concentration and effect of duration on chelation of metal ions. Similar study was conducted with copper ions. Besides volumetric analysis, gravimetric analysis and flame atomic mass spectroscopy were employed for characterization. Due to presence of above mentioned functional groups, chitosan has high affinity for different

classes of dyes. The work was extended to study the removal efficiency of chitosan for acid and direct dyes. The quantitative evaluation was based on optical method governing the Beer Lamberts law using spectrophotometer.

5.2 MATERIALS AND METHODS

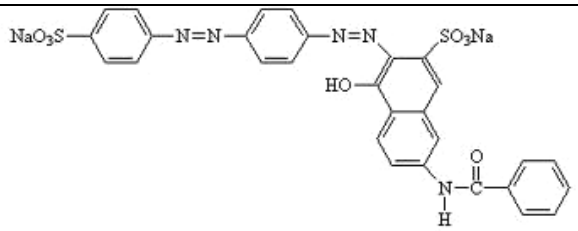
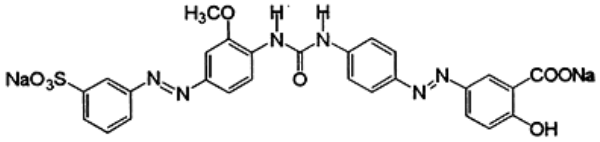
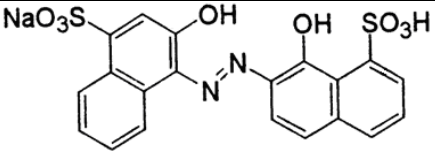
5.2.1 Fabric

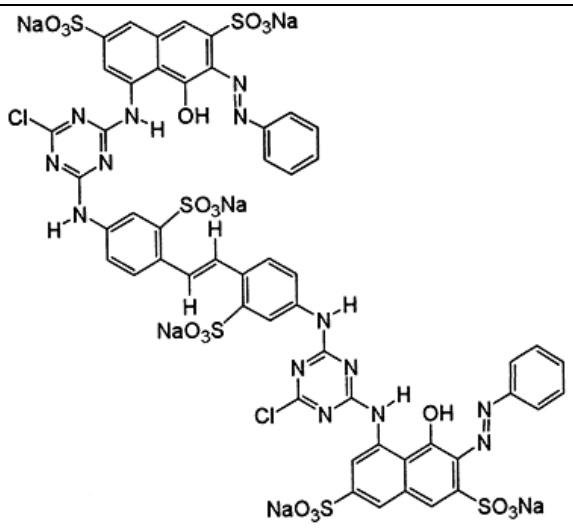
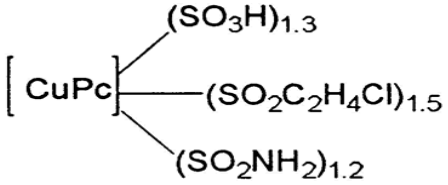
100% grey cotton fabric (warp and weft count 40s) was procured from Mafatlal Industries Ltd, Nadiad, Gujarat State and scoured/ bleached fabric as described in section 2.2.1(chapter 2).

5.2.2 Dyes and chemicals

The details of various dyes and chemicals employed in present research investigation are given in Table 5.2.

Table 5.2 Specifications of various dyes and chemicals

Sr. No	Name and Supplier	Specifications
1.	C.I.Direct Red 81 Colourtex Industries Ltd, Gujarat State, India.	 • Mol wt. 675.6
2.	CI Direct Yellow 44 Colourtex Industries Ltd, Gujarat State, India.	 • Mol wt 634.53
3.	C.I. Acid Blue 158 Colourtex Industries Ltd, Gujarat State, India.	 • Mol wt 495.45

4.	C.I. Reactive Red 152 Colourtex Industries Ltd, Gujarat State, India.	 • Mol wt 1572.12
5.	C.I. Reactive Blue 25 Colourtex Industries Ltd, Gujarat State, India.	
6.	Chitosan • CHT MC (Marine Chemicals, Cochin, Kerala) • CHT (Mahtani Chitosan Pvt. Ltd., Veraval, Gujarat) • CHT-D3(Synthesized by depolymerization of CHT as per method in section 2.2.4, chapter 2) • TMCHT1 &TMCHT3 (Quaternized derivative synthesized from CHT as per method described in section 4.2.3, chapter 4) • CHTN4 & CHTN5 (Syntheised from CHT as per method described insection	DAC: 89.03%, Molecular weight: 654,127; Viscosity: 180 cPs DAC: 90%, Molecular weight: 135,839; Viscosity: 22 cPs Molecular weight: 38,733 Degree of quaternization: TMCHT1:13.41% and TMCHT3: 50.92 Particle size: CHTN4: 408.73 nm and CHTN5: 534.2

	3.2.5, chapter 3)	
7.	Activated Charcoal S. D. Fine-Chem Ltd.,Thane, Maharastra State	Particle Size: 300 nm, Methylene Blue Adsorption (0.15% Solution) 270 mg/g

Other reagents like disodium salt of ethylene diamine tetraacetic acid (Na_2EDTA), tetrasodium salt of ethylene diamine tetraacetic acid (Na_4EDTA), sodium thiosulphate ($Na_2S_2O_3$), potassium iodide (KI), sodium hydroxide (NaOH), soda ash (Na_2CO_3), sodium sulphate (Na_2SO_4), sodium silicate (Na_2SiO_4), Calcium chloride ($CaCl_2$), copper sulphate ($CuSO_4.5H2O$), hydrogen peroxide (H_2O_2), dimethyl formamide (DMF), N-Methyl 2-pyrolidone (NMP) [$C_4H_6N(CH_3)O$] etc used were of analytical grade obtained Qualikem Fine Chemicals Pvt Ltd, Vadodara. Double distilled water was employed for all synthesis and analytical purposes. Anionic detergent (Ezee) was obtained from Godrej Consumers Products Ltd, Mumbai.

5.2.3 Hydrogen peroxide bleaching of cotton fabric

Scoured cotton fabric was treated with solution containing hydrogen peroxide (30%) 10 g/L, soda ash 10 g/L sodium silicate 10 g/L, detergent 1 g/L at about 85 ^{0}C for 60 minutes. The material-to-liquor ratio was maintained at 1:30. After bleaching was over, the fabric was given hot wash at 80 ^{0}C for 20 minutes and then rinsed.

5.2.4 Dyeing with direct dyes

The same method was employed as described in section 2.2.7, chapter 2.

5.2.5 Treatment of water containing calcium ions with chitosan derivatives

A stock solution of calcium chloride corresponding to Ca^{+2} ions concentration of 2500 mg/L was prepared by dissolving $CaCl_2$ (10 g) in distilled water (1000 ml) in a volumetric flask. After mixing the chitosan (1g) with distilled water was acidified with acetic acid (1.5 ml/L) to dissolve the chitosan and then mixed with 100 ml of calcium chloride stock solution. The solution was diluted to about 950 ml, allowed react for required time and then treated with few drops of 10% sodium hydroxide solution to

precipitate out the chitosan and the diluted to 1000 ml. The solution was the filtered and the filtrate was analyzed for Ca^{+2} ions content by EDTA titrimetric method. A blank titration of solution containing 100 ml of stock solution of calcium chloride diluted to 1000 ml with distilled water (corresponding to Ca^{+2} ions concentration of 250 mg/L) was also conducted for the evaluation of initial concentration of calcium ions.

5.2.6 Treatment of water containing Cu(II) ions with chitosan derivatives

A stock solution of 15 g/L of $CuSO_4.5H_2O$ was prepared in presence of 0.5 g/L sulphuric acid to get a clear solution. After mixing the chitosan (1g) with distilled water was acidified with acetic acid (1.5 ml/L) to dissolve the chitosan and then mixed with 100 ml of Copper sulphate stock solution. The solution was diluted to about 950 ml, allowed react for required time and then treated with few drops of 10% sodium hydroxide solution to precipitate out the chitosan and the diluted to 1000 ml. The solution was the filtered and the filtrate was analysed for Cu(II) ions content iodometrically. A blank titration of solution containing 100 ml of stock solution of sulphate diluted to 1000 ml with distilled water (corresponding to Cu(II) ions concentration of 394.32 mg/L) was also conducted for the evaluation of initial concentration of Cu(II)ions.

5.2.7 Treatment of dye waste water (effluent) with chitosan derivatives

Required amount of dye stock solution (to set final concentration of 25 mg/L of dye) was taken in a 1000 ml volumetric flask and 1g chitosan was added and diluted to the mark. Stirred gradually for required dwell time and filtered. The filtrate was analysed spectrometrically for the dye content. In case of acidic medium, 1g predissolved chitosan in 100ml water containing 1.5 ml acetic acid was added in dye solution and diluted to about 900 ml. Stirred well and after a dwell time of treatment; the system was neutralized by adding few drops of 10% sodium hydroxide solution to precipitate out the chitosan. The solution was made to 1L and filtered. The filtrate was analysed for dye content.

5.2.8 FTIR analysis

FTIR of chitosan and metal ion-chitosan complex samples were determined using described in section 2.2.11, chapter 2

5.2.9 Atomic Absorption Spectroscopy

This method is applicable for the determination of various heavy metal such as copper, chromium, lead, nickel etc. Presence of metal ions in treated solution and on adsorbent was determined by using Varien AA140/240/280 atomic absorption spectrophotometer in air-acetylene flame at Pollucon laboratories Pvt Ltd, Surat. The standard method employed for the examination was AAS-APHA (Edition 21, 2005) 3111B.

5.2.10 Determination calcium ions in water by EDTA titrimetric method

Exactly 50 ml of aliquot/sample was taken in conical flask and made alkaline by addition of 2ml of 1N NaOH solution into it. A pinch (0.1- 0.2 g) of Eriochrome Black T was the added into above solution to produce red wine colour. The solution in conical flask was then immediately titrated with 0.02N Na_2EDTA till the purple or bluish colour is produced. Calcium ions content was determined using equation (5.1) and the chelation efficiency from equations (5.2) and (5.3) [41].

$$\text{Calcium content, mg/L (as } Ca^{+2}) = \frac{ml\ of\ EDTA\ titrant \times 1 \times 1000}{ml\ of\ sample taken\ for\ titration} X\ 0.40 \qquad \textbf{(5.1)}$$

[1 ml of 0.02N EDTA ≡ 1 ml of $CaCO_3$]

$$\text{Chelation efficiency in terms of sorption of } Ca^{+2} \text{ ions by chitosan (mg/g)} = \frac{I_0 - I_F}{M} \qquad \textbf{(5.2)}$$

$$\text{Chelation efficiency in terms of } Ca^{+2} \text{ ions removal from water (mg/L)} = I_0 - I_F \qquad \textbf{(5.3)}$$

Where, I_0 is the initial concentration (mg/L) of Ca^{+2} ions and I_F is the concentration (mg/L) of Ca^{+2} ions in treated water. M is the concentration of chitosan (g/L).

5.2.11 Measurement of pH of liquor

The pH of solution was determined using pocket size pH meter (Hanna Instruments, Model HI96107)

5.2.12 Iodometric method for determination of Cu(II) ions

100 ml aliquot (sample solution) was taken in a conical flask and mixed with 10 ml of 10% liquor ammonia to obtain a dark blue colour. The solution was then neutralized with acetic acid; a slight excess acid was added, followed by 2 g of potassium iodide. The flask was placed in dark for about 15 minutes for complete liberation of free iodine and the solution then titrated against 0.1N sodium thiosulphate using starch indicator. Ammonium thiocyanate (2 g in 10 ml water) was then added and titration continued. The amount of Cu(II) present in the given solution can be calculated from the equation (5.4) and the chelation efficiency from equations (5.5) and (5.6) [41].

$$\text{Cu(II) ions content, mg/L} = \frac{A \times 6.36 \times 1000}{V} \qquad \textbf{(5.4)}$$

Where, *A* is the ml of 0.1N $Na_2S_2O_3$ titrant (burette reading) and
V is the ml of sample of sample taken for titration (100 ml)

$$\text{Chelation efficiency in terms of sorption of Cu(II) ions by chitosan (mg/g)} = \frac{I_0 - I_F}{M} \qquad \textbf{(5.5)}$$

$$\text{Chelation efficiency in terms of copper ions removal from water (mg/L)} = I_0 - I_F \qquad \textbf{(5.6)}$$

Where, I_0 is the initial concentration (mg/L) of Cu(II) ions and I_F is the concentration(mg/L) of Cu(II) ions in treated water. M is the concentration of chitosan (g/L).

5.2.13 Gravimatric analysis of adsorbent-metal complex

The recovered precipitate after washing thoroughly with distilled water was collected in ash less filter paper (Whatman Filter Paper No 41). The precipitate along

with the filter paper taken in accurately weighed silica crucible was incinerated in muffle furnace (Tempo Instruments & Equipments (P) Ltd, Mumbai, Model No 502) at 800 ^{0}C for 5 h. The weight of crucible containing ash was taken for the calculation of ash content.

The ash was mixed with 1-2 drops of concentrated sulphuric acid, dissolved in distilled water and diluted to 1L. The aliquot was analysed for Cu (II) content iodometrically as described in section 5.2.13.

5.2.14 Purification and strength determination of direct and acid dyes

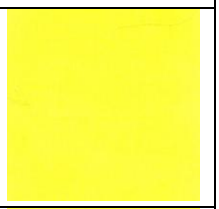
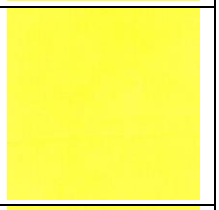
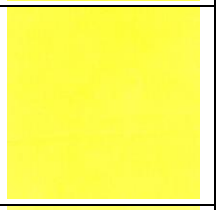
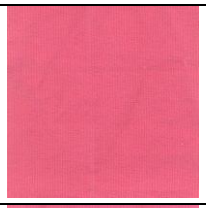
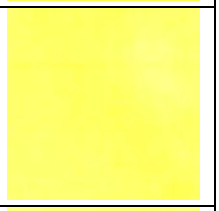
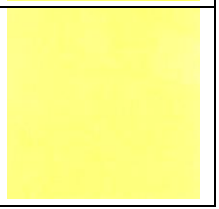
Commercial grade anionic dye (i.e. direct dye or acid dye) was mixed with dimethyl formamide (DMF) at 60^{o}C to dissolve the dye portion leaving the inorganic additive undissolved. The solution was filtered through filter paper (Whatman Filter Paper No 41, pore size 0.45µm) and the filtrate was subjected to oven drying at 130^{o}C to evaporate the solvent. The purified dye was used for testing and for spectrophotometric analysis to prepare calibration curve. To prepare calibration curve, a stock solution of dye (1000 mg/L) was prepared by dissolving 100 mg of dye in 100 ml distilled water. This solution was used for preparation of dye solutions of different concentrations namely 10, 20, 30, 40 50 mg/L etc. by dilution. The optical densities (absorbance) ware measured on visible spectrometer (Systronics visible spectro 105). Before analyzing the dye solution, the absorbance was set to zero for water. The linear plot of absorbance (optical density) versus concentration was used to determine the concentration of dye in solutions.

5.3. RESULTS AND DISCUSSION

5.3.1 Chelation study with calcium ions

Calcium in water is mostly present as salts such as chloride, sulphate, bisulphate, bicarbonate etc. Its presence in water is highly essential to human health especially for the growth of bone. However, the excess of it causes detrimental effects on kidneys. The presence of calcium ions together with magnesium ions imparts hardness to water. Excess presence of salts of such alkaline earth metals is undesired in various industrial operations. Boilers, heat exchangers and similar industrial plants frequently become

scaled up with insoluble deposits derived from water hardness salts such as calcium sulphate, carbonate or phosphate and seriously affect their efficiency [1, 41].

$CaCl_2$ content in dye bath, mg/L	C.I.Direct Red 81	C.I. Direct Yellow 44
Control		
50		
100		
1000		
5000		

Dye 1% o.w.m

Figure 5.1 Effect of calcium ions in dyebath on colour value of direct dyed cotton fabric

The presence of excess amount of such ions is also undesirable in water used in textile processing. The scaly structure of wool fibre affords room for the deposition of calcium soaps formed with hard water. This imparts harshness to the fibre. Hard water increases the breakage of silk reeling. Surface characteristics raw silk such as colour and lustre are also affected due to the deposition of calcium salts when degumming is carried out in hard water. Presence of calcium ions and other heavy metal ions in water is highly detrimental in the production of rayon. In the manufacture of low ash content rayon, the

water of practically zero ppm hardness is the prime requirement [42]. Calcium ions form insoluble salts with fatty acid soaps and hence impair the detergency power of soaps. Subsequently these insoluble complexes are firmly retained on the fibre surface thus affecting the performance of the scoured material. These deposits act as barrier for dye penetration and produce patchy dyeings [1, 43]. Several dyes have shown anomalous behaviour in presence of calcium and magnesium ions. Hard water is especially detrimental to vat dyeing operations often produces off shades and patchy dyeings. Calcium ions cause agglomeration of disperse dyes due to complex formation of dispersing agent present with dyes. This problem is often found with dark shades such as coffee (Coralene Brown 3BS), Navy blue (C.I. Disperse Blue 79), black etc in low MLR dyeing machines. The detrimental effect of calcium ions, for example, on the dyeing of C.I.Direct Red 81 and C.I. Direct Yellow 44 is illustrated in Figure 5.1 and in Table 5.3.

Table 5.3 Effect of calcium ions content in dyebath on colour value of direct dyed cotton fabric

$CaCl_2$ content in dyebath, mg/L	**C.I. Direct Red 81**				**C.I. Direct Yellow 44**			
	K/S	**Value of colour spacing coordinate**		**Look**	**K/S**	**Value of colour spacing coordinate**		**Look**
		a	**b**			**a**	**b**	
Control	9.00 *(100)*	46.34	11.76,	Bright	5.35 *(100)*	2.33	74.55	Bright
50	8.49 *(94)*	45.76	10.02,	Bright	5.08 *(95)*	1.71	74.54	Bright
100	8.46 *(94)*	43.63	10.27	Bright	4.88 *(88)*	1.73	73.89	Dull
1000	7.84 *(87)*	38.89	8.72	Bright	4.11 *(77)*	1.87	73.55	Dull
5000	4.50 *(50)*	32.74	4.63	Dull	3.12 *(58)*	1.88	73.03	Dull

Dye 1% o.w.m, Values in parentheses indicate colour strength in percentage
a= Redder, -a = Greener; b= Yellower, -b= Bluer

Most of the hard water is conventionally softened by ion exchange method, wherein calcium (and magnesium) ions are exchanged with sodium ions. This is commonly referred as ‘Cation exchange softening’ or ‘Zeolite softening’. The effluent which is discharged into streams is mostly subjected to ‘lime-soda softening’ treatment

[1, 42]. However, the fresh and recycled water used for textile processing such as scouring & bleaching, dyeing, printing etc containing calcium and other water hardening ions is treated with sequestering or chelating agents such as EDTA, NTA or phosphate compounds. Here the metallic ions are not removed from the bath but are inactivated by the reaction with chelating agent and prevent their deleterious effects on fabrics [5, 44]. In order to get an idea of the chelation property of chitosan in its different forms as listed in Table 5.4 were examined and their performance was compared with tetra sodium salt of ethylene diamine tetra acetic acid (Na_4EDTA).

Table 5.4 Chitosan derivatives employed for chelation study

Sample	Chemical Name	Properties			
		DAC, %	Molecular weight	Particle size, nm	Degree of quaternization, %
CHT-MC	Chitosan	89.03	654,127	-	-
CHT	Chitosan	90	135,839	4014	-
CHT-D3	Chitosan	90	38,733	-	-
CHTN4	Nano-chitosan	-	135,839	408.73	-
CHTN5	Nano-chitosan	-	135,839	534.2	-
TMCHT1	Trimethyl chitosan chloride	-	-	-	13.41
TMCHT3	Trimethyl chitosan chloride	-	-	-	50.92

5.3.1.1 Characterization and mechanism of chelation of calcium ions on chitosan

The structural changes in chitosan after on Ca^{+2} ions adsorption was studied using FTIR spectra. Chitosan in acidic medium was treated with calcium chloride for a known reaction time and then recovered by sodium hydroxide precipitation. The residue was washed thoroughly with distilled water until neutral and then oven dried and analysed for FTIR spectrometry. The FTIR spectra so taken of CHT and CHT-Ca complex (chelated residue) are shown in Figures 5.2.

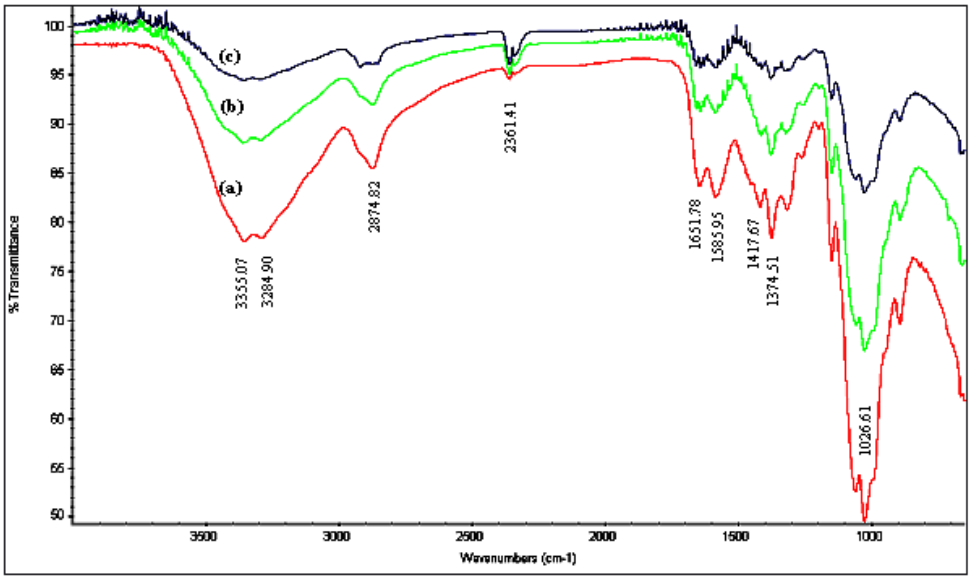
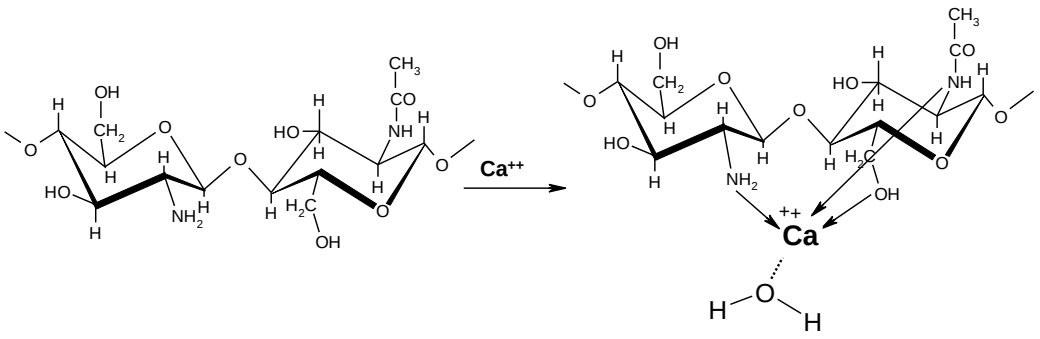


Figure 5.2 FTIR spectra of CHT and CHT-Ca complex residues: (a) CHT, (b) CHT-Ca, treatment time, 24h and (c) CHT-Ca, treatment time 96h

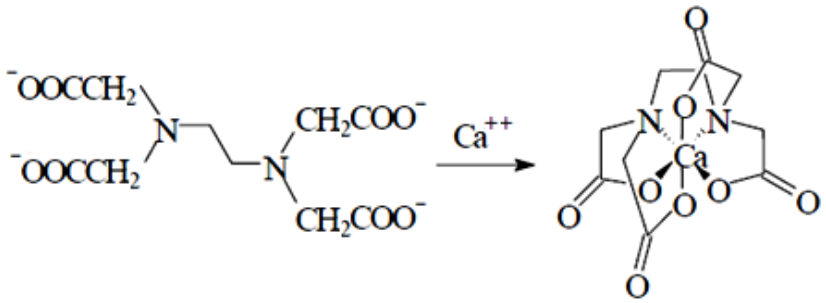
The FTIR spectrum of parent chitosan, Figure 5.2(a), shows the characteristic broad band at wave numbers 3355, 3284cm^{-1} are mainly attributed to O-H, NH and NH_2 stretch and the absorption peak at 2874 cm^{-1} is due to the C - H symmetrical and unsymmetrical stretch. The absorption band at 1651 cm^{-1} is assigned to C=O (carbonyl) stretching of secondary (amide I) amide bond/group, which is characteristic of N-acetyl group and the medium peak at 1585 cm^{-1} is due to bending vibrations of N-H of amide II bond (N-acetyl residue) and the primary amine. Another medium absorption peak at 1374 cm^{-1} characterizes the N-H of amide III bonds. A strong absorption peak at 1025 cm^{-1} is due to primary hydroxyl group, characteristic peak of $-CH_2OH$ in primary alcohols, arised from C-H stretching [45-48]. Spectra (b) and (c) show progressive modifications in absorption peaks due to complex formation with Ca^{+2} ions. The broadening of the peak at 3355 cm^{-1} and progressive reduction of peak at wave number at 1025cm^{-1} indicate the involvements of amino and hydroxyl groups in the scavenging of the calcium ions. Prolong treatment (96h) results in changes in amide I (1651 cm^{-1}) and amide II (1585 cm^{-1}) and amide III (1374 cm^{-1}) peaks characterizes interactions of these groups with calcium ions. Thus in general, the chelation of calcium with chitosan is effected due the lone pair of electrons donation from hydroxyl and unprotonated amino groups of chitosan. The possible reaction of chelation can be illustrated by scheme 5.1. A similar kind of

interaction of oxygen and nitrogen of EDTA with calcium ions through the donation of lone pair of electrons is shown in scheme 5.2.



Chitosan Ca^{+2}-Chitosan complex

Scheme 5.1 Chelation of calcium ions by chitosan



$(EDTA^{4-})$ $(CaEDTA^{2-})$

Scheme 5.2 Chelation of calcium ions by EDTA

5.3.1.2 Effect of structural modification of chitosan on chelation of calcium ions

The binding of calcium ions to chelating agents is normally effected through ionic linkages or semi polar (coordinate) linkages [49]. The chelation property of chitosan may be attributed the electron donating property of nitrogen and oxygen atoms present in its structure. Thus the structural aspects of chitosan which get influenced by factors like degree of deacetylation, molecular weight, chemical modifications etc is believed to influence its metal binding property. Chelation efficiency of chitosan derivatives for calcium ions, as a function treatment time, in terms of residual ions in water determined

using equation 5.1 is shown Table 5.5 and in terms of sorption by chitosan derivatives, determined using equation 5.2, is shown in Table 5.5 in graphically in Figure 5.3.

Table 5.5 Effect of chelation time on residual Ca^{+2} ions in water

Treatment time	Residual Ca^{+2} ions content (I_F, mg/L) in water treatment with :				
	Na_4EDTA	**CHT-MC**	**CHT**	**CHT-D3**	**TMCHT3**
15 mins	143.60	229.76	229.20	221.76	244.00
30 mins	143.20	208.00	203.60	192.80	243.60
45 mins	142.20	193.36	186.40	183.60	242.16
60 mins	142.00	186.93	181.60	178.41	242.00
2 h	142.00	179.20	177.20	177.04	241.84
3 h	141.76	177.84	176.80	176.8	241.60
4 h	141.76	177.60	176.80	176.8	241.20
6 h	141.76	177.20	176.40	176.56	241.20
24 h	140.40	173.10	175.20	176.60	240.80
48 h	140.32	171.60	176.00	176.40	239.44
72 h	140.00	165.60	176.4	176.48	237.76

Initial conc of calcium ions in water was (I_0) 250 mg/L, pH 3.5, conc of chelating agent 1g/L
Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; CHT-D2=71, 676; CHT-D3=38,733; DQ of TMCHT3: 50.92%

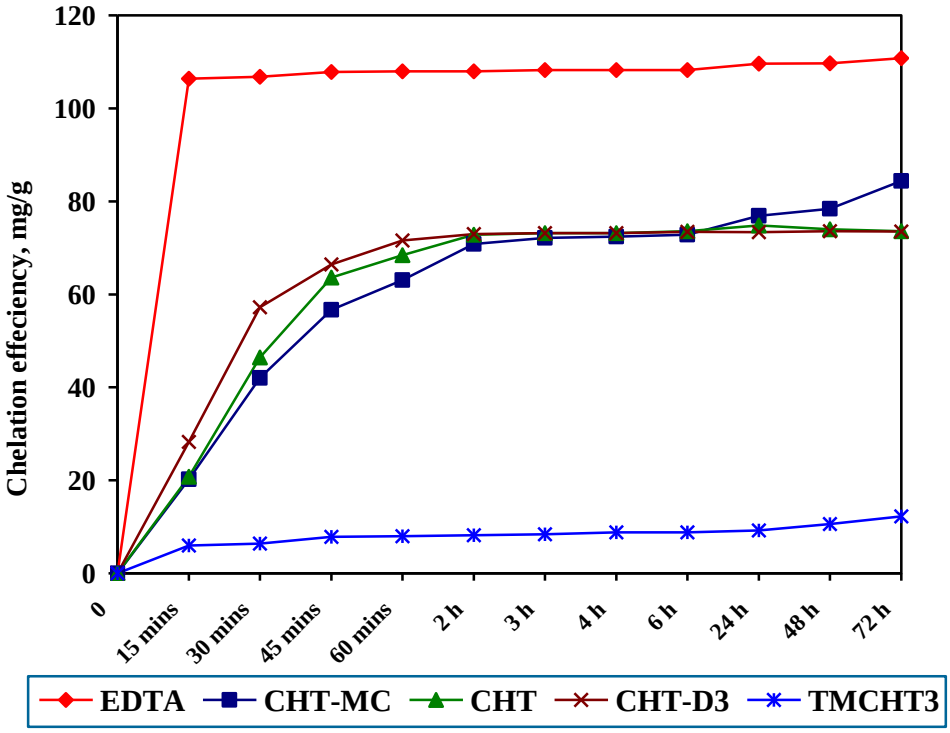
Table 5.6 Effect of treatment time on extent of chelation of Ca^{+2} ions by different chelating agents

Treatment time	Chelated Ca^{+2} ions (mg/g) from water treated with:				
	Na_4EDTA	**CHT-MC**	**CHT**	**CHT-D3**	**TMCHT3**
15 min	106.40	20.24	20.8	28.24	6.00
30 min	106.80	42.00	46.4	57.20	6.40
45 min	107.80	56.64	63.6	66.40	7.84
60 min	108.00	63.03	68.4	71.59	8.00
2 h	108.00	70.80	72.8	72.96	8.16
3 h	108.24	72.16	73.2	73.20	8.40
4 h	108.24	72.40	73.2	73.20	8.80
6 h	108.24	72.80	73.6	73.44	8.80
24 h	109.60	76.90	74.8	73.40	9.20
48 h	109.68	78.40	74.0	73.60	10.56
72 h	110.76	84.40	73.6	73.52	12.24

Conc of chelating agent 1g/L, Initial conc of calcium ions in water (I_0) was250 mg/L, pH 3.5
Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; DQ of TMCHT3= 50.92%

The chelation efficiency of EDTA, as observed from Table 5.6 (Figure 5.3), was maximum and attained the equilibrium rapidly. Prolong treatment showed negligible or very slight improvement in further removal of calcium ions indicating the saturation of chelation. In case of chitosan, the scavenging process was slower and was somewhat influenced by its molecular weight. At the onset and for the first 60 minutes of treatment, the rate of chelation was slightly higher for low molecular weight chitosan. It means, for the first 60 minutes of treatment, low molecular weight chitosan (CHT-D3) was more effective. When the treatment was continued for 2 to 4 hrs, the calcium ion sorption was almost of same level for different molecular weight chitosans. With increase in molecular weight of chitosan (CHT-MC), the rate of sorption of calcium ions was slowed down but the absolute adsorption after prolong treatment (>6 h) was higher and the equilibrium was not reached even after 96 hrs of treatment. Thus, the influence of molecular weight of chitosan seems to be slightly more pronounced on the rate of sorption rather than on absolute sorption of calcium ions.TMCHT3 i.e. quaternized chitosan derivative was found to be ineffective in chelation property.

A substantially higher chelation capacity of EDTA may be attributed to the combined effect of ionic linkages of calcium cations with anionic carboxylate groups and the coordinate bonds with amino groups as shown in scheme 5.2. The electrostatic attraction between EDTA and calcium ions and their high mobility may be the driving force for the attachments. Chitosan, on the other hand, is a polymeric material having rigid conformation. When dissolved in water in presence of acid, most of the amino groups are protonated and therefore are incapable of bonding with calcium cations. The only possible route of interaction is through hydroxyl groups and/or N-acetyl groups. Further, these polycationic macromolecules in solutions are mostly swollen entangled bunches exposing very small surface area and hence provide less ligands for interaction with metal ions. The chitosan molecules, therefore, are slower in chelation than EDTA.



Conc of chelating agent 1g/L, Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, CHT-D2=71,676, CHT-D3=38,733.DQ of TMCHT3: 50.92%

Figure 5.3 Effect of treatment time on extent of chelation of Ca^{+2} ions by different chelating agents

The extent of accessible interactive part of the ligands is determined by the physical state of macromolecules in solvent which in turn is determined by its molecular size and hence the molecular weight. Low molecular weight chitosans (CHT-D3) in solution are comparatively more discrete and extended due to less intra and intermolecular forces and thus provide more surface area for chelation reactions and therefore shows enhanced rate of sorption. Conversely, high molecular weight chitosan (CHT-MC) molecules in solution are more entangled and provide fewer sites for interaction and hence results in to low rate of sorption. On prolong treatment, large sized chitosan molecules under go depolymerization due to hydrolysis and/or disentanglement [50, 51] leading to uncovering of sites and continued chelation without reaching the equilibrium. Results of trimethyl chloride (TMCHT3) were discouraging. This may be ascribed to the absence of free amino groups for coordination with metal ions and also to the presence of bulkier methyl groups acting as barrier for diffusion of metal ions.

Another reason for retarded entry of metal cations into quaternized chitosan may be the presence of permanent cations causing the ionic repulsion.

5.3.1.3 Effect of concentration of chitosan derivatives on chelation of calcium ions

Another important parameter that influences the sorption of metal ions is the concentration of chelating agent. However the concentration of chitosan is believed to alter the chain conformation and/or physical state in solution and also the viscosity, as discussed in chapter 2. Further the aqueous behaviour of chitosan solution was found to be governed by storage period. These properties may be responsible for the extent of chelating sites/ligands available for metal binding. Thus, in order to understand chelation behaviour of chitosans, the effect of concentration of different molecular weights of chitosans for short (1h) and long duration (24 h) on sorption calcium ions were studied. The corresponding results determined using equation 5.1 for 1 h and 24 h treatments for the residual Ca^{+2} ions in treated water are shown in Table 5.7 and Table 5.9 respectively. And the effect of concentration on chelation efficiency in terms of Ca^{+2} ions removal from treated water, determined using equation 5.3, is presented in Table 5.8 and Table 5.10 and graphically in Figure 5.4 and Figure 5.5 respectively.

Table 5.7 Residual Ca^{+2} ions content in treated water as a function of concentration of chelating agent for 1h treatment

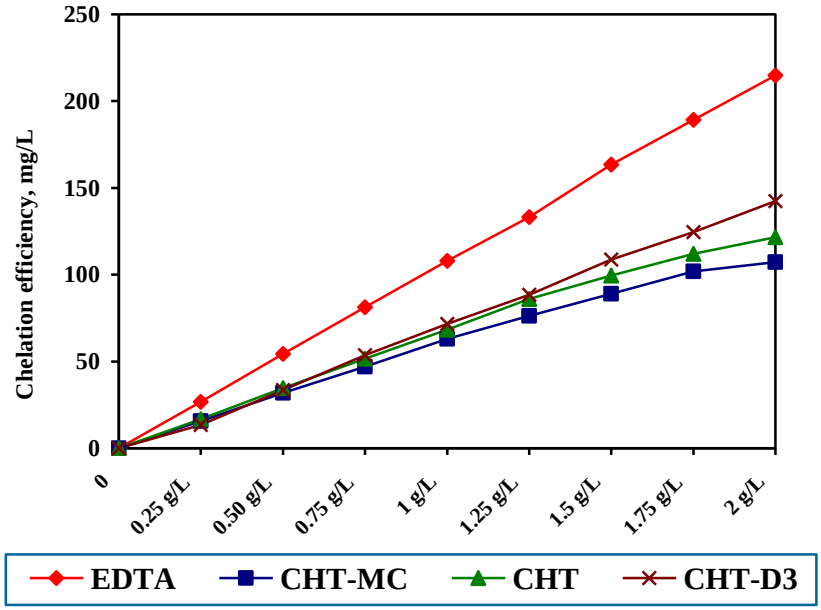
Conc, g/L	**Residual Ca^{+2} ions content in water (I_F, mg/L) after treatment with:**			
	Na_4EDTA	**CHT-MC**	**CHT**	**CHT-D3**
0.25	223.20	234.40	233.20	236.61
0.50	195.60	218.16	215.36	216.52
0.75	168.80	203.07	198.40	196.37
1.00	142.00	186.93	181.60	178.41
1.25	116.80	173.76	164.00	161.57
1.50	86.56	161.20	150.56	141.29
1.75	60.80	148.16	138.00	125.44
2.00	35.20	142.64	128.40	107.64

Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, CHT-D3=38,733,
Initial concentration of Ca^{+2} ions in liquor was (I_0)250 mg/L, pH 3.5, Treatment time 1h

Table 5.8 Effect of concentration of chelating agents on the extent of removal of Ca^{+2} ions for 1h treatment

Conc, g/L	Ca^{+2} ions, mg/L, removed from water treated with:			
	Na_4EDTA	CHT-MC	CHT	CHT-D3
0.25	26.80 *(10.7)*	15.60 *(6.2)*	16.80 *(6.7)*	13.39 *(5.4)*
0.50	54.40 *(21.8)*	31.84 *(12.7)*	34.64 *(13.9)*	33.48 *(13.4)*
0.75	81.20 *(32.5)*	46.93 *(18.8)*	51.60 *(20.6)*	53.63 *(21.5)*
1.00	108.00 *(43.2)*	63.03 *(25.2)*	68.40 *(27.4)*	71.59 *(28.6)*
1.25	133.20 *(53.3)*	76.33 *(30.5)*	86.00 *(34.4)*	88.43 *(35.4)*
1.50	163.44 *(65.4)*	88.91 *(35.6)*	99.44 *(39.8)*	108.71 *(43.5)*
1.75	189.20 *(75.7)*	101.85 *(40.7)*	112.00 *(44.8)*	124.56 *(49.8)*
2.00	214.80 *(85.9)*	107.25 *(42.9)*	121.60 *(48.6)*	142.36 *(56.9)*

Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, CHT- D3=38,733, Initial conc of Ca ions in liquor was (I_0)250 mg/L, pH 3.5, Values in parenthesis indicate chelation efficiency in terms of % removal



Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; CHT-D3=38,733

Figure 5.4 Effect of concentration of chelating agents on the extent of removal of Ca^{+2} ions for 1h treatment

Table 5.9 Residual Ca^{+2} ions content in treated water as a function of concentration of chelating agent for 24h treatment

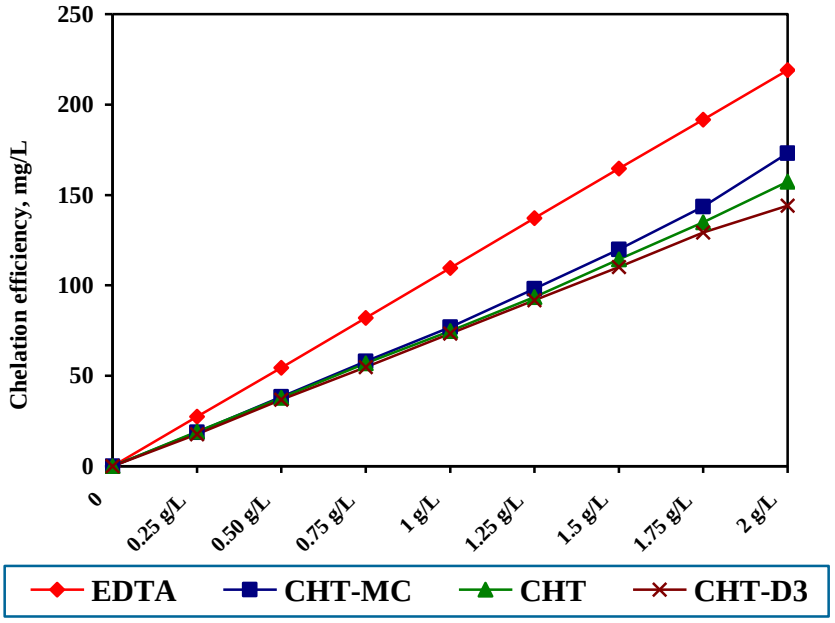
Conc, g/L	Residual Ca^{+2} ions content in water (I_F, mg/L) after treatment with:			
	Na_4EDTA	**CHT-MC**	**CHT**	**CHT-D3**
0.25	222.58	231.21	230.93	232.32
0.50	195.52	211.55	212.22	213.26
0.75	167.94	191.93	193.12	195.17
1.00	140.40	173.10	175.20	176.60
1.25	112.78	151.92	156.48	158.27
1.50	85.41	130.04	135.56	139.82
1.75	58.36	106.35	115.17	120.75
2.00	30.87	75.90	92.62	105.84

Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; CHT-D3=38,733, Initial conc of Ca^{+2} ions in liquor was (I_0) 250 mg/L, pH 3.5

Table 5.10 Effect of concentration of chelating agents on the extent of removal of Ca^{+2} ions for 24h treatment

Conc, g/L	Ca^{+2} ions, mg/L, removed from water treated with:			
	Na_4EDTA	**CHT-MC**	**CHT**	**CHT-D3**
0.25	27.42 *(10.9)*	18.79 *(7.5)*	19.07 *(7.6)*	17.68 *(7.1)*
0.50	54.48 *(21.8)*	38.45 *(15.4)*	37.78 *(15.1)*	36.74 *(14.7)*
0.75	82.06 *(32.8)*	58.07 *(23.2)*	56.88 *(22.8)*	54.83 *(21.9)*
1.00	109.60 *(43.8)*	76.90 *(30.8)*	74.80 *(29.9)*	73.40 *(29.4)*
1.25	137.22 *(54.9)*	98.08 *(39.2)*	93.52 *(37.4)*	91.73 *(36.7)*
1.50	164.59 *(65.8)*	119.96 *(48.0)*	114.44 *(45.8)*	110.18 *(44.1)*
1.75	191.64 *(76.7)*	143.65 *(57.5)*	134.83 *(53.9)*	129.25 *(51.7)*
2.00	219.13 *(87.7)*	173.10 *(69.2)*	157.38 *(62.9)*	144.16 *(57.7)*

Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; D3=38,733; Initial conc of Ca ions in liquor was (I_0)250 mg/L, pH 3.5, Values in parenthesis indicate chelation efficiency in terms of % removal



Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; CHT- D3=38,733

Figure 5.5 Effect of concentration of chelating agents on the extent of removal of Ca^{+2} ions for 24h treatment

It was observed from Table 5.8 and Table 5.10 (Figure 5.4 and Figure 5.5) that the sorption curve for EDTA followed linearity with respect to concentration and almost same level of chelation efficacy observed for both the durations of treatment. The sorption of calcium ions was found to be increased with increase in concentration of chitosan derivatives. The chelation behaviour of chitosan derivatives, however, was observed to be anomalous in context to molecular weight of chitosan and duration of treatment. In first hour of treatment or for short treatment of time as depicted in Figure 5.4, the sorption curve for low molecular weight chitosan (CHT-D3) was also almost linear. In case of high molecular weight chitosans, some deviations in sorption capacity were noticed at higher concentrations. The efficiency of Ca^{+2} removal was found to be reduced at higher concentration which was more prominent in CHT-MC. Further, it was observed that the chelation efficiency decreased with increase in the molecular weight of chitosan i.e. in the order of CHT-D3>CHT>CHT-MC. On prolong treatment i.e. when the treatment was extended to 24 h, as demonstrated in Figure 5.5, the chelation behaviour of chitosan was significantly altered particularly for high molecular weight chitosans. The sorption behaviour of low molecular weight chitosan (CHT-D3) was not

much influenced except slight improvement in it but behaviour was entirely changed when the molecular weight was increased. A slightly upward trend in sorption of metal ions from water was noticed when the concentrations of high molecular weight chitosans were increased. The order in degree of sorption by chitosan with respect to molecular weight was, however, reversed as against short duration of treatment. The extent of sorption of calcium ions now increased with increase in molecular weight i.e. in the order of CHT-MC>CHT>CHT-D3.

Low molecular weight chitosans (CHT-D3) in solution are comparatively more free and extended due to less intra and intermolecular forces and thus provide more surface area for chelation reactions and therefore shows enhanced sorption. High molecular weight chitosan (CHT-MC) molecules in solution, on the other hand, are more entangled due to overlapping of macromolecules and therefore provide fewer sites for interaction resulting in to decreased sorption. On prolong treatment, high molecular weight chitosans may under go depolymerization due to hydrolysis and/or disentanglement [50, 51] leading to uncovering of sites for chelation. In all cases, increase in concentration obviously leads to increased sites and the chelation extent. Studies related to viscosity behaviour in chapter 2 revealed that the high molecular weight chitosans, during the short duration of treatments, are still in aggregated state due to entanglement and overlapping at increased concentration may contribute to reduced chelation.

5.3.1.4 Effect of pH on chelation of calcium ions

Aqueous dissolution of chitosan is accomplished with the protonation of amino groups on polymer macromolecule by the added acid. The amount of added acid and hence the pH of the solution is believed to determine the extent of protonation of amino groups of chitosan and also the physical state of chitosan in solution. In order to study the effect of pH on chelation efficiency of CHT, three sets of series of CHT in calcium chloride systems were prepared. In first set of series (pH 3.5), the system was acidified with sufficient quantity of acetic acid (1.5 ml/L) to ensure complete dissolution of CHT. In second set of series (pH 5.5), the system was acidified with only an optimum amount of acetic acid (0.7 ml/L) for dissolution of CHT. The systems, after the dwell time, were

neutralized with concentrated sodium hydroxide solution to precipitate out the CHT- Ca complex and the supernant liquors were analysed for calcium ions content. Third set of series was heterogeneous where in the CHT was treated with calcium chloride solution at neutral pH. The residual Ca^{+2} ions present in treated water, determined using equation 5.1, at different pH is illustrated in Table 5.11 and the effect of pH of the solution on the chelation efficiency of CHT (determined using equation 5.2) is presented in Table 5.12 and graphically in Figure 5.6.

It was observed that the chelation efficiency of CHT was maximum at pH 5.5 followed by at pH 3.5. The chelation efficiency of undissolved CHT i.e. at neutral pH was found to be meager or almost negligible. Since the attachment of calcium ions with chitosan is possible through the co-ordinate bonds by the donation of lone pair of electrons of amino, acetamido and hydroxyl groups. However, in highly acidic medium i.e. at pH 3.5 most of the amino groups are believed to be protonated and their involvement in such bond formation is less probable. In this situation the scavenging of calcium ions would be attributed to hydroxyl and *N*-acetyl groups.

Table 5.11 Residual Ca^{+2} ions content in CHT treated water at different pH

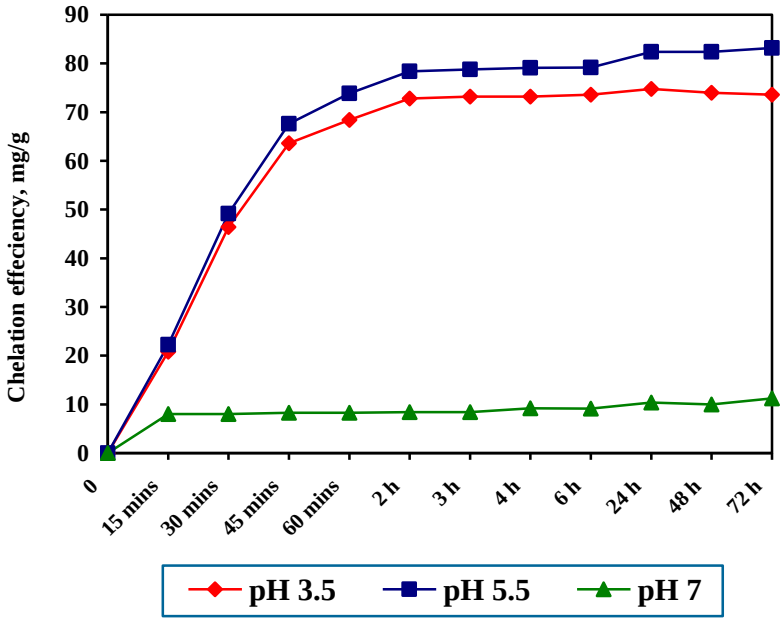
Treatment time	**Residual Ca^{+2} ions content in water (I_F, mg/L) after treatment with CHT at:**		
	pH= 3.5 (Homogeneous system)	**pH= 5.5 (Homogeneous system)**	**pH= 7 (Heterogeneous system)**
15 min	229.20	227.76	242.00
30 min	203.60	200.80	242.00
45 min	186.40	182.40	241.76
60 min	181.60	176.16	241.76
2 h	177.20	171.60	241.60
3 h	176.80	171.20	241.60
4 h	176.80	170.88	240.80
6 h	176.40	170.80	240.90
24 h	175.20	167.60	239.60
48 h	176.00	167.60	240.00
72 h	176.4	166.8	238.80

Mol wt of chitosan: CHT=135,839; Conc of CHT 1g/L, Initial conc of calcium ions in water was (I_0) 250 mg/L

Table 5.12 Effect of pH of CHT solution on extent of chelation of Ca^{+2} ions from water

Treatment time	Chelated Ca^{+2} ions, mg/g, from water treated at:		
	pH= 3.5 (Homogeneous system)	pH= 5.5 (Homogeneous system)	pH= 7 (Heterogeneous system)
15 min	20.8	22.24	8
30 min	46.4	49.2	8
45 min	63.6	67.6	8.24
60 min	68.4	73.84	8.24
2 h	72.8	78.4	8.4
3 h	73.2	78.8	8.4
4 h	73.2	79.12	9.2
6 h	73.6	79.2	9.1
24 h	74.8	82.4	10.4
48 h	74	82.4	10.0
72 h	73.6	83.2	11.2

Mol wt of chitosan: CHT=135,839; Conc of CHT 1g/L, Initial conc of calcium ions in water (I_0) was 250 mg/L



Conc of CHT 1g/L

Figure 5.6 Effect of pH of CHT solution on chelation efficiency measured in terms sorption of Ca^{+2} ions from water

At slightly higher pH (pH 5.5), some fraction of amino groups remain unprotonated or free. The free amino groups, due to the presence of lone pair of electrons, must be capable of forming co ordinate linkages with calcium ions and hence somewhat enhanced chelation was noticed at pH 5.5. In both of these cases, the CHT molecules in solution are in extended form and the functional groups on them are accessible to calcium ions. However, chitosan is insoluble in water at neutral pH very less surface area and also functional groups are disposed for the scavenging reaction and therefore are reflected by poor chelation efficacy.

5.3.1.5 Effect of particle size of chitosan on chelation of calcium ions

The number of ligands (reactive sites) on chitosan macromolecule available for chelation of metal ions can be increased by increasing the surface area which in turn can be conveniently increased by scaling down the particle size to nano level. A detailed study on synthesis of nano chitosan (CHTN) dispersion is discussed in chapter 3. In brief; the ionotropic gelation technique of chitosan with sodium tripolyphosphate (TPP) was employed for the synthesis of nano chitosan dispersions. The varying levels of particle size of near nano chitosan, for a given molecular weight chitosan, were obtained by changing the concentration of the polymer (chitosan). Two different near nano chitosans of average particle sizes 408.73 nm and 534.2 nm, considered for present experiment, were obtained from CHT at concentrations 1.5 g/L and 2 g/L respectively. These stocks solutions were employed for chelation study of calcium ions at concentration 1g/L, obtained by dilution. The residual Ca^{+2} ions present in nano chitosan treated water, determined using the equation 5.1, is presented in Table 5.13. The effect of particle size on the chelation efficiency of chitosan, determined using the equation 5.2, is shown in Table 5.14 and graphically in Figure 5.7.

The results revealed that the rate of chelation enhanced by the reduction in particle size of chitosan indication the faster establishment of equilibrium. Further, the absolute chelation value at equilibrium was found to be increased. Besides increased surface area, the presence of phosphorous (P) in TPP can also act as a ligands for scavenging calcium ions [49].

Table 5.13 Effect of particle size of CHT on chelation efficiency measured in terms of residual Ca^{+2} ions in water

Treatment time	Residual Ca^{+2} ions content in water (I_F, mg/L) treated with:		
	CHT (Particle size 4014 nm)	CHTN4 (Particle size 408.73nm)	CHTN5 (Particle size 534.2nm)
15 min	229.20	185.61	193.29
30 min	203.60	176.33	181.17
45 min	186.40	172.71	175.78
60 min	181.60	171.78	173.54
2 h	177.20	171.49	171.47
3 h	176.80	171.63	171.24
4 h	176.80	170.69	170.88
6 h	176.40	170.58	170.64
24 h	175.20	168.07	168.63

Initial conc of calcium ions in water (I_0) was 250 mg/L, conc of chelating agent 1g/L

Table 5.14 Effect of particle size of CHT on extent of Ca^{+2} ions chelated

Treatment time	Chelated Ca^{+2} ions (mg/g) from water treated with:		
	CHT (Particle size 4014 nm)	CHTN4 (Particle size 408.73nm)	CHTN5 (Particle size 534.2nm)
15 min	20.80	64.39	56.71
30 min	46.40	73.67	68.83
45 min	63.60	77.29	74.22
60 min	68.40	78.22	76.46
2 h	72.80	78.51	78.53
3 h	73.20	78.37	78.76
4 h	73.20	79.31	79.12
6 h	73.60	79.42	79.36
24 h	74.80	81.93	81.37

Initial conc of calcium ions in water was (I_0) 250 mg/L, conc of chelating agent 1g/L

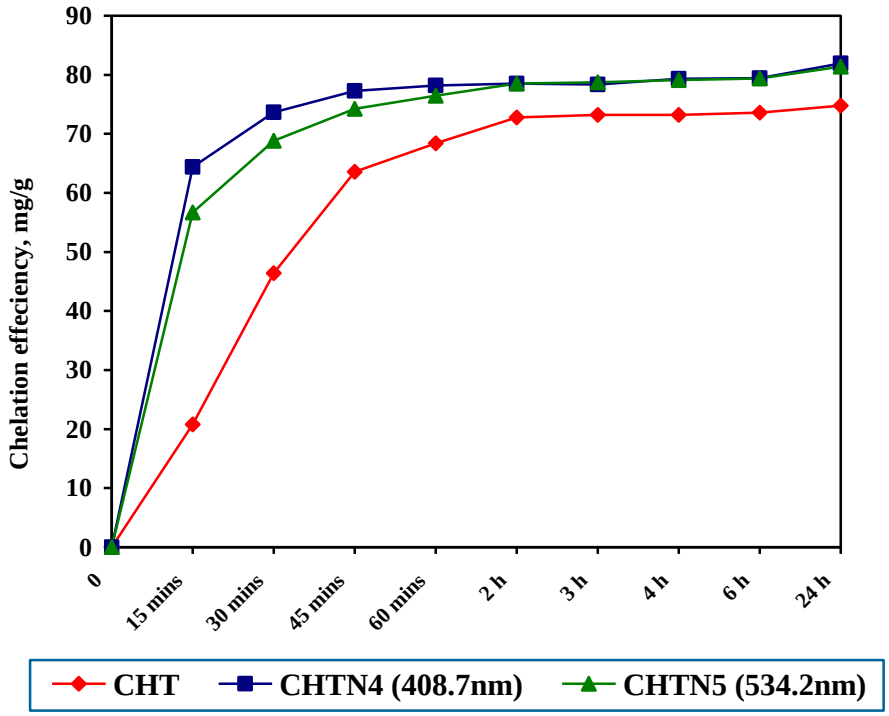


Figure 5.7 Effect of particle size on chelation efficiency of CHT for calcium ions

5.3.2 Chelation study with copper ions

Copper belongs to IB group of periodic table having atomic number 29. It is widely distributed in nature as the free metal and more commonly, as compounds in various ores such as cuprite (Cu_2O), chalcopyrite ($CuS{\cdot}FeS$), azurite [$Cu(OH)_2{\cdot}2CuCO_3$] and malachite $Cu_2CO_3(OH)_2$. There are also deposits of cupric chloride and cupric arsenide. It is commonly found in drinking water as complexes such as $[CuCO_3(aq)]^0$, $[Cu(CO_3)_2]^{2-}$, $[CuOH]^+$, $[Cu(OH)_3]^-$ and $[Cu(OH)_4]^{2-}$ [49,52]. Low levels (generally below 20µg/L) can derive from rock weathering. Some industrial contamination also occurs, but the principle sources in water supplies are corrosion of brass and copper pipe and addition of copper salts during water treatment of algal control. Copper is also a constituent of several dyes and pharmaceutical preparations. Copper content in textile and allied industries effluent was found to be up to 77 mg/L as against the WHO norms 0.05 mg/L (Table 5.1) [1,41, 53]. Traces of copper (5-45 µg/L) in under ground water and about 110 mg/kg of soil in and around Surat were detected [54]. Presence of copper in drinking water and edibles is a nutritional requirement. Deficiency of copper can lead to

reproductive abnormalities. A safe and adequate copper intake of 2-3 mg/day in supply water may be practical. Excess amounts of copper in various substances may be vital, objectionable or perhaps indicative of contamination or malfunction. Copper traces promote rancidity and off-flavors in foods and beverages. Chronic copper poisoning causes gastrointestinal catarrh and aemochromatosis [55]. Presence of copper in water can seriously affect the performance of various unit operations of textile processing such as desizing, scouring, bleaching, dyeing etc. Hence it is advised to avoid copper/brass fittings especially in bleaching plants. Copper is found to be adsorbed by enzyme molecules to form complexes and inactivate the enzymatic action. Copper exhibits a catalytic action on hydrogen peroxide decomposition. Presence of copper is reported to cause instability in peroxide bleaching baths and damage the cotton during bleaching. The bleaching efficiency in terms of whiteness is also reported to be seriously affected, in absence of peroxide stabilizers. Copper is highly undesirable in woolen processing also, as it is readily absorbed on wool. In the bleaching of wool, copper catalyzes the reaction with hydrogen peroxide to the extent that holes are formed in the material. Presence of copper ions causes deleterious effect on the colour of various dyes used for cellulose, nylon and protein fibres; nevertheless it enhances the wash and light fastness properties [5, 43, 44].The deleterious effect of Cu(II) ions observed on hydrogen peroxide bleaching of scoured cotton fabric is shown in Table 5.15 and direct and reactive dyeing of cotton in Table 5.16 A and Table 5.16B respectively and in Figure 5.8.

Table 5.15 Effect Cu(II) ions in hydrogen peroxide bleach bath on bleaching of cotton fabric

$CuSO_4$ content in bleach bath, mg/L	**W.I.**	**Y.I.**	**B.I.**
Control	88.40	1.33	78.08
100	85.98	4.29	73.02
200	85.06	4.69	71.17
500	84.14	5.58	69.32

*Scoured sample***:** *W.I. = 78.07, Y.I. = 17.02 and B.I. =56.91*

Table 5.16A Effect of Cu(II) ions content in dye bath on colour value of direct dyed cotton fabric

$CuSO_4$ content in dye bath, mg/L	C.I. Direct Red 81				C.I. Direct Yellow 44			
	K/S	Value of colour spacing coordinate		Look	K/S	Value of colour spacing coordinate		Look
		a	b			a	b	
Control	8.99 *(100)*	46.34	11.76	Bright	5.35 *(100)*	2.33	74.55	Bright
50	7.90 *(88)*	32.16	2.99	Dull	5.41 *(101)*	2.41	72.01	Bright
100	7.30 *(81)*	27.06	-0.06	Dull	5.28 *(98)*	2.49	69.82	Dull
200	7.28 *(81)*	46.34	11.76	Bright	5.35 *(100)*	2..61	56.31	Dull

Dye 1% o.w.m, a= Redder, -a = Greener; b= Yellower, -b= Bluer
Values in parentheses indicate colour strength in percentage

Table 5.16B Effect of Cu(II) ions content in dye bath on colour value of reactive dyed cotton fabric

$CuSO_4$ content in dye bath, mg/L	C. I. Reactive Red 152				C. I. Reactive Blue 25			
	K/S	Value of colour spacing coordinate		Look	K/S	Value of colour spacing coordinate		Look
		a	b			a	b	
Control	4.35 (100)	44.40	-9.96	Bright	4.71 (100)	-28.37	-20.73	Bright
50	4.21 (97)	43.84	-10.98	Dull	4.33 (92)	-27.56	-17.73	Bright
100	3.167 (73)	41.11	-10.60	Dull	4.08 (87)	-27.28	-15.76	Dull
200	3.66 (84)	36.25	-13.29	Dull	3.89 (83)	-28.77	-21.88	Dull

Dye 1% o.w.m, a= Redder, -a = Greener; b= Yellower, -b= Bluer
Values in parentheses indicate colour strength in percentage

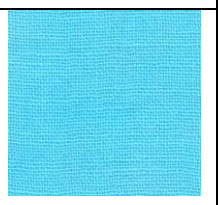
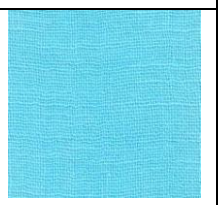
$CuSO_4$ content in dye bath, mg/L	C.I.Direct Red 81	C.I. Direct Yellow 44	C.I. Reactive Red 152	C.I. Reactive Blue 25
Control				
50				
100				
200				

Figure 5.8 Effect of Cu (II) ions in the dye bath on the dyeing of cotton using direct and reactive dyes

5.3.2.1 Characterization and mechanism of chelation of Cu (II) ions on chitosan

The structural changes in chitosan occurred due to Cu (II) ions adsorption can be conveniently studied using FTIR spectra analysis. Chitosan in acidic medium was treated with copper sulphate for a known reaction time and then recovered by sodium hydroxide precipitation. The residue was washed thoroughly with distilled water until neutral and then oven dried. The FTIR spectra of CHT and CHT-Cu complex (chelated residue) so taken are presented in Figure 5.9 and Figure 5.10.

Important ligands on chitosan macromolecule that form complex with metal ions are oxygen pertaining to primary and secondary hydroxyl groups and nitrogen belonging to amino and acetamido groups. The broad bands at wave numbers 3355, 3284cm^{-1} are mainly attributed to O-H, NH and NH_2 stretch.

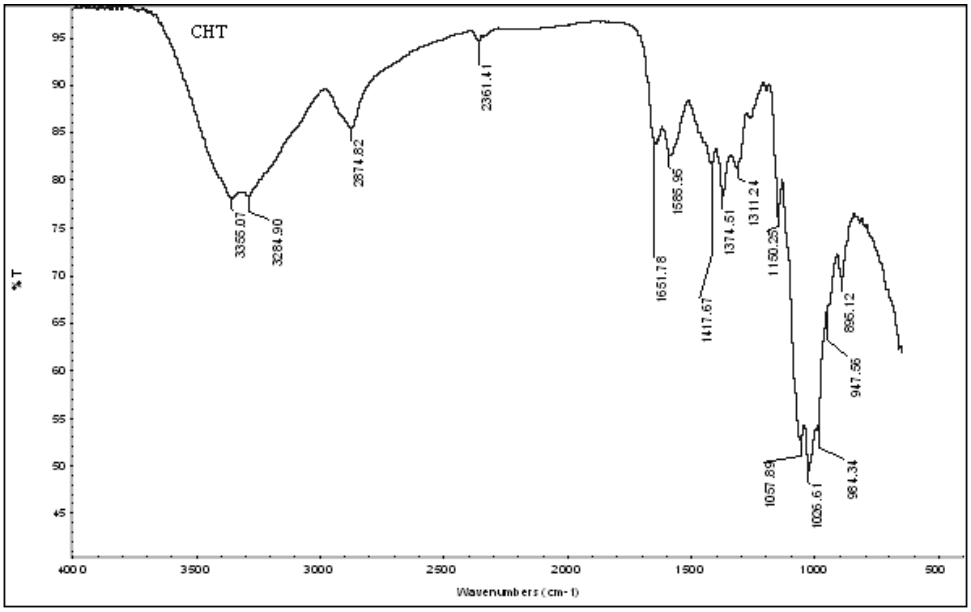


Figure 5.9 FTIR spectrum of CHT

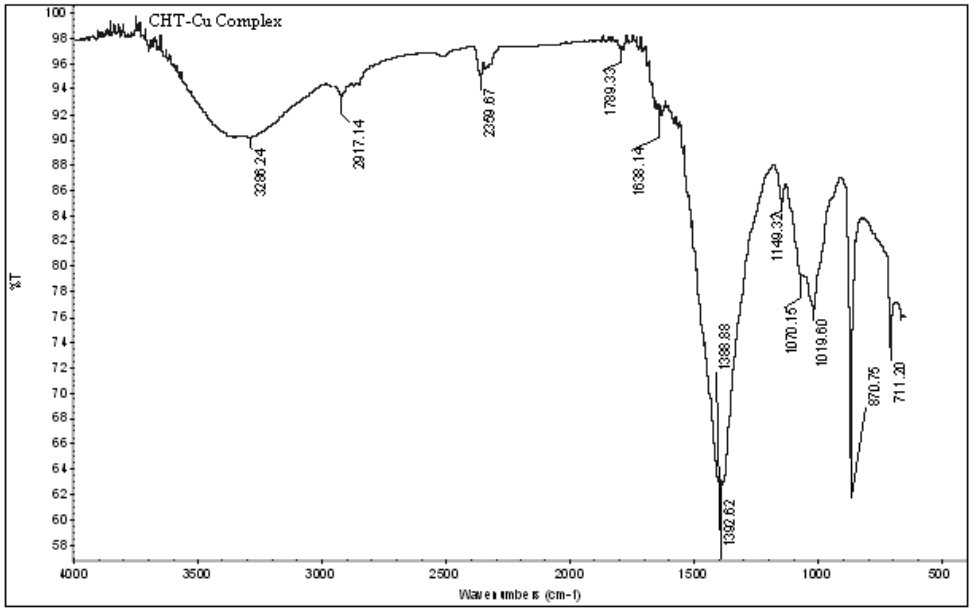
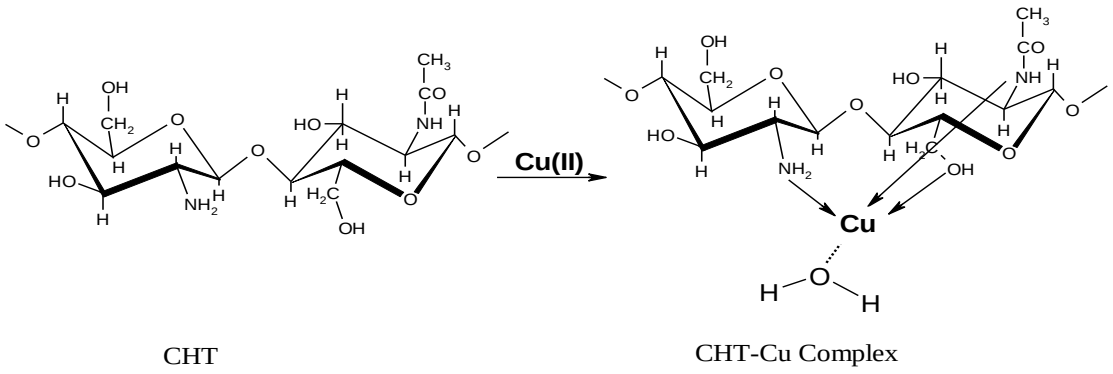


Figure 5.10 FTIR spectrum of CHT-Cu complex residue

The absorption band at 1651 cm^{-1} is assigned to C=O (carbonyl) stretching of secondary (amide I) amide bond/group, which is characteristic of N-acetyl group and the medium peak at 1585 cm-1 is due to bending vibrations of N-H of amide II bond (N-acetyl residue) and the primary amine. Another medium absorption peak at 1374 cm^{-1} characterizes the N-H of amide III bonds. A strong absorption peak at 1025 cm-1 is due

to primary hydroxyl group, characteristic peak of -CH_2OH in primary alcohols, arised from C-H stretching [45-48]. The structural changes in chitosan arised due to complex formation with copper ions are presented in spectrum as shown in Figure 5.10. The broadening of the peak at 3355 cm^{-1} and progressive reduction of peak at wave number at 1025cm^{-1} indicate the involvements of amino and hydroxyl groups in the scavenging of the Cu(II) ions. Modifications in amide I (1651 cm^{-1}) and amide II (1585 cm^{-1}) and amide III (1374 cm^{-1}) and the formation of new peak at 1392 cm^{-1} due to deformations in amide groups characterize interactions of these groups with copper ions [46, 56]. Thus in general, the scavenging of Cu(II) with chitosan is effected due the lone pair of electrons donation from hydroxyl and amino and amido groups of chitosan. The possible ways of Cu(II) binding by chitosan proposed by different authors are illustrated by scheme 5.3.



Scheme 5.3 Cu (II) ions binding by chitosan

5.3.2.2 Quantitative evaluation of Cu (II) ions

The most commonly method employed for the determination of Cu(II) ions content in a given solution or on adsorbent is the atomic absorption spectroscopy. The experiment was performed by the treatment of adsorbent sample (e.g. CHT) 1g/L with copper sulphate corresponding to Cu(II) 300 mg/L in presence of acetic acid (0.7 g/L, pH 5.5) with constant stirring to ensure complete dissolution of CHT. After specified treatment time (24 h in present experiment) the adsorbent was precipitated using few ml of 10% sodium hydroxide solution and the level was made to 1litre with distilled water. The filtrate and precipitate (recovered by filtration) were analysed.

$$2CuSO_4 + 4KI \longrightarrow 2CuI + I_2 + 2K_2SO_4$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_2O_6$$

Scheme 5.4 Reactions involved in iodometry

Alternatively, Cu (II) was also determined iodometrically [41]. This method is based on principle that the oxidation of iodides (KI) to iodine takes place by Cu(II) ions and Cu(II) ions get reduced to Cu(I) ions in acidic pH. The liberated iodine can be titrated with standard sodium thiosulphate solution. The over all reactions of iodometry are shown in scheme 5.4 and the residual Cu(II) ions content in treated water can be calculated using the equation 5.4 and the chelated Cu(II) ions by chelating agents using the equation 5.5.

The recovered precipitate can also be analysed for the determination of extent of copper ions sorption by the adsorbent e.g. CHT. The experiment is performed through gravimetric analysis method. The precipitate is thoroughly washed with distilled water and collected in ashless filter paper and subjected to incineration in muffle furnace at 800 ^oC for about 5 h to obtain ash of constant weight. The ash is then analysed iodometrically as discussed above by dissolving in water using a drop of concentrated sulphuric acid. A comparative results for residual Cu(II) ions content in treated water determined by different analytical methods is given in Table 5.17 and the sorption on different chitosans by above three methods is summerized in Table 5.18.

Table 5.17 Residual Cu(II) ions content in treated water determined by various analytical methods

Chelating agent	**Residual Cu(II) ions content in treated water (I_F, mg/L)**	
	Analytical methods	
	AAS	**Iodometry**
CHT	3.685	5.088
CHT-MC	0.248	Not detected

Conc of chelating agent 1g/L, pH 5.5, Treatment time 24 h, Initial conc of Cu(II) in water I_0 (mg/L) determined by: AAS 300, Iodometry 297.65

Table 5.18 Chelation of Cu(II) ions by chelating agents determined by various analytical methods

Chelating agent	Chelated Cu(II) ions by chelating agents (mg/g)		
	Analytical methods		
	AAS	Iodometry	Gravimetry*
CHT	296.32	292.56	284.93
CHT-MC	299.75	292.56	286.20

Conc of chelating agent 1g/L, pH 5.5, Treatment time 24 h, Initial conc of Cu(II) in water, I_0 (mg/L) determined by: AAS 300, Iodometry 297.65,
**The ash obtained from the precipitate of adsorbent-Cu complex was analyzed iodometrically*

Results from Table 5.17 and Table 5.18 revealed that the atomic absorption spectrometric method was the most sensitive and could be able to detect a very small concentrations of Cu(II) ions. The iodometric titration method also gave comparable results and was able to detect Cu (II) ions down at 5 mg/L concentration. Gravimetric method shown slightly lesser values, which may be due losses during the collection of precipitate and desorption of copper ions during repeated washing. In order to precise detection of Cu(II) ions at lower levels of concentrations, the initial concentration, here after, was maintained higher i.e. 394.32 mg/L by using copper sulphate 1.5 g/L solution. Atomic absorption spectrometric method was needed outsourcing, nevertheless accurate, was employed for analysis of selected samples. Iodometric method was used for other samples.

5.3.2.3 Effect of structural modification of chitosan on chelation of Cu (II) ions

The ability of copper ions binding of chitosan is believed to be dependent on the availability of number of electron donating ligands such as *O* and *N*. The state of these ligands on chitosan macromolecules is anticipated to alter due to chemical modifications. The residual Cu(II) ions in treated water, determined using equation 5.4, is given in Table 5.19. Thus the Cu(II) ions sorption by chitosan derivatives as a function of structural modifications, calculated using equation 5.5, is shown in Table 5.20 and graphically in Figure 5.11. The results were compared against a common sequestering agent like ethylene diamine tetra acetic acid (Na_4EDTA).

Table 5.20 and Figure 5.11 illustrate that EDTA attained the equilibrium rapidly for the Cu(II) ions binding and the chelation capacity was maximum. The prolong treatment showed very slight improvement in further removal of Cu(II) ions indicating the saturation of chelation. During the iodometric evaluation of Cu(II) ions in EDTA treated solution, a continuous liberation of iodine was observed when the solution was stored for few minutes after the titration with sodium thiosulphate was over. This may be due to desorption of copper ions from carboxylate groups of EDTA by ion exchange with protons in highly acidic iodomeric reaction medium.

Table 5.19 Residual Cu (II) ions content in different chelating agent treated water as a function of chelation time

Treatment time	Residual Cu(II) ions content (mg/L) in water treated with:					
	Na_4EDTA	CHT-MC	CHT	CHT-D3	TMCHT1	TMCHT3
15 min	81.41	328.81	310.37	276.67	326.27	351.07
30 min	77.89	228.96	211.79	185.71	258.27	329.45
45 min	71.23	151.37	141.19	138.01	174.36	311.64
60 min	70.60	129.11	120.84	132.29	148.19	302.10
90 min	68.07	122.11	116.39	124.02	145.64	297.65
2 h	63.60	119.27	115.75	122.75	146.28	284.29
3 h	58.51	106.21	111.30	115.75	135.47	258.85
4 h	52.79	100.49	106.21	111.30	119.57	248.04
24 h	38.16	95.40	100.49	103.67	108.12	218.15

Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; CHT-D3=38,733; DQ: TMCHT1= 13.41%, TMCHT3= 50.92%, Conc of chelating agent 1g/L, Initial conc of Cu(II) ions (I_0) was 394.32 mg/L, pH 5.5

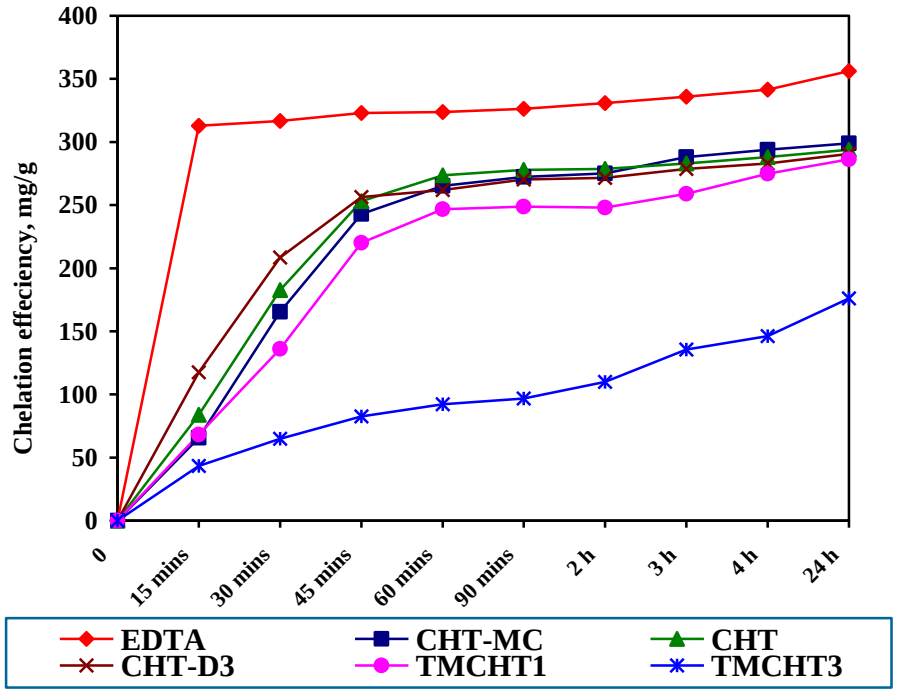
The chelation behaviour chitosan and trimethyl chitosan towards copper ions was found to be almost similar to that of calcium ions except extent of sorption capacity which was enhanced for copper ions. The chelation process of chitosan was slower and influenced, somewhat, by its molecular weight. At the onset and in first hour of treatment, the rate of chelation was slightly higher for low molecular weight chitosan. It means, in the first hour of treatment, low molecular weight chitosan (CHT-D3) was more

effective. When the treatment was continued for 1 to 2 h, the copper ion sorption was almost at same level for different molecular weight chitosans. The rate of adsorption by high molecular weight chitosan (CHT-MC) for Cu(II) ions was slowed down but the absolute adsorption after prolong treatment (>3 hrs) was higher. Thus, the influence of molecular weight of chitosan seems to be slightly more pronounced on the rate of sorption rather than on absolute sorption of copper ions. Modification of chitosan by quaternization process was found to deprecate metal binding capacity. The chelation capacity of trimethyl chitosan chloride (TMCHT) was decreased with increase in degree of quaternization. The chelation efficacy of TMCHT, however, was somewhat more effective for Cu(II) binding than Ca^{+2} ions binding.

Table 5.20 Effect of treatment time on extent of chelation of Cu (II) ions by different chelating agents

Treatment time	**Chelated Cu(II) ions (mg/g) from water treated with:**					
	Na_4EDTA	**CHT-MC**	**CHT**	**CHT-D3**	**TMCHT1**	**TMCHT3**
15 min	312.91	65.51	83.95	117.65	68.05	43.25
30 min	316.73	165.36	182.53	208.61	136.10	64.87
45 min	323.09	242.95	253.13	256.31	220.06	82.68
60 min	323.72	265.21	273.48	262.03	246.64	92.22
90 min	326.27	272.21	277.93	270.30	248.64	96.67
2 h	330.72	275.05	278.57	271.57	248.04	110.03
3 h	335.81	288.11	283.02	278.57	258.85	135.47
4 h	341.53	293.83	288.11	283.02	274.75	146.28
24 h	356.16	298.92	293.83	290.65	286.20	176.17

Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, CHT-D3=38,733. DQ: TMCHT1= 13.41%, TMCHT3= 50.92%, Conc of chelating agent 1g/L, Initial conc of Cu(II) ions (I_0) was 394.32 mg/L, pH 5.5



Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; CHT-D3=38,733; DQ: TMCHT1= 13.41%, TMCHT3= 50.92%, Conc of chelating agent 1g/L

Figure 5.11 Chelation behaviour of chitosan derivatives for Cu(II) ions

The enhanced tendency of complex formation of chelating agents with copper ions may be explained with the help of its electronic configuration. Copper, though not strictly termed as transition metals as their *d* orbitals are complete, still they form a number of complexes when their ions have incomplete *d* orbitals e.g. in the case of Cu(II) ions having the coordination numbers are usually 2,4,and 6 [49]. A substantially higher chelation capacity of EDTA may be attributed to the combined effect of ionic linkages of Cu(II) cat ions with anionic carboxylate groups and the coordinate bonds with amino groups. The electrostatic attraction between EDTA and metal cat ions and their high mobility may be the driving force for the attachments. Chitosan, on the other hand, is a polymeric material having rigid conformation. When dissolved in water in presence of acid, most of the amino groups are protonated and therefore are incapable of bonding with metal cations. The only possible route of interaction is through unprotonated amino groups, hydroxyl groups and/or N-acetyl groups. Further, these polycationic macromolecules in solutions are mostly swollen entangled bunches exposing very small

surface area and hence provide fewer sites for the interaction with metal ions. The chitosan molecules, therefore, are slower in chelation than EDTA.

The extent of accessible interactive ligands is determined by the physical state of macromolecules in solvent which in turn is determined by its molecular size and hence the molecular weight. Low molecular weight chitosans (CHT-D3) in solution are comparatively more discrete and extended due to less intra and intermolecular forces and thus provide more surface area for chelation reactions and therefore shows enhanced rate of sorption. Conversely, high molecular weight chitosan (CHT-MC) molecules in solution are more entangled and provide fewer sites for interaction and hence results in to low rate of sorption. On prolong treatment, large sized chitosan molecules under go depolymerization due to hydrolysis and/or disentanglement [50, 51] leading to uncovering of sites and continued chelation without reaching the equilibrium. Results of trimethyl chitosan chloride (TMCHT) were discouraging. This may be ascribed to the absence of free amino groups for coordination with metal ions and also to the presence of bulkier methyl groups acting as barrier for diffusion of metal ions.

5.3.2.4 Effect of pH on chelation of Cu (II) ions

An important parameter that alters the state of ligands on chitosan and its derivatives is the pH of the medium. Acidic pH is highly essential for dissolution of chitosan in aqueous medium. The acidic pH, however, leads to protonation of amino groups depressing the metal binding property. In order to understand the effect of pH on chelation behaviour of CHT and its quaternized derivative TMCHT3, two different pH for each were selected namely pH 3.5 (acetic acid 1.5 ml/L) and pH 5.5 (acetic acid 0.7 ml/L). Higher pH (pH ~7) was avoided due to the formation of hydroxides of copper which causes precipitation [49]. The residual Cu(II) ions content in CHT and TMCHT treated water, determined using equation 5.4, at different pH is presented in Table 5.21 and the sorption of Cu(II) ions by these derivatives, determined using equation 5.5, as a function of pH in Table 5.22 and graphically in Figure 5.12.

Table 5.21 Residual Cu (II) ions content in CHT derivatives treated water as a function of pH

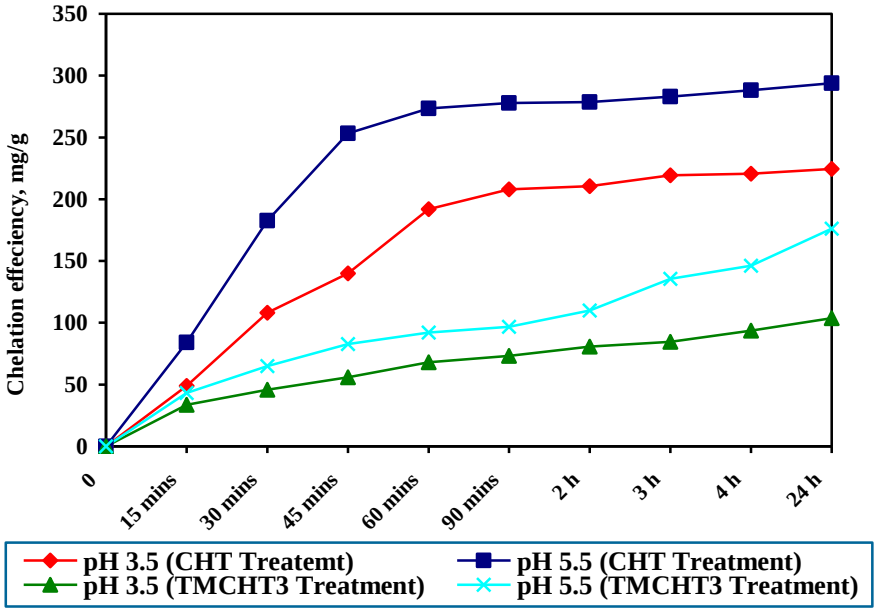
Treatment time	Residual Cu(II) ions content (I_F, mg/L) in water treated with:			
	CHT		TMCHT3	
	pH= 3.5	pH= 5.5	pH= 3.5	pH= 5.5
15 min	345.35	310.37	360.61	351.07
30 min	286.20	211.79	348.53	329.45
45 min	254.40	141.19	338.35	311.64
60 min	202.25	120.84	326.27	302.10
90 min	186.35	116.39	321.81	297.65
2 h	183.67	115.75	313.55	284.29
3 h	174.90	111.30	309.73	258.85
4 h	173.63	106.21	300.83	348.04
24 h	169.81	100.49	290.65	218.15

Mol wt of chitosan: CHT=135,839; DQ: TMCHT3= 50.92%, pH 5.5,
Conc of chelating agent 1g/L, Initial concentration of Cu(II) ions (I_0) was 394.32 mg/L

Table 5.22 Effect of pH of chitosan derivatives solution on extent of chelation of Cu(II) ions

Treatment time	Chelated Cu(II) ions (mg/g) from water treated with:			
	CHT		TMCHT3	
	pH= 3.5	pH= 5.5	pH= 3.5	pH= 5.5
15 min	48.97	83.95	33.71	43.25
30 min	108.12	182.53	45.79	64.87
45 min	139.92	253.13	55.97	82.68
60 min	192.07	273.48	68.05	92.22
90 min	207.97	277.93	73.14	96.67
2 h	210.65	278.57	80.77	110.03
3 h	219.42	283.02	84.59	135.47
4 h	220.69	288.11	93.76	146.28
24 h	224.51	293.83	103.67	176.17

Mol wt of chitosan: CHT=135,839; TMCHT3= 50.92%, pH 5.5,
Conc of chelating agent 1g/L, Initial conc of Cu(II) ions (I_0) was 394.32 mg/L



Mol wt of chitosan: CHT=135,839, DQ: TMCHT3= 50.92%, Conc of chelating agent 1g/L, Initial conc of Cu (II) ions (I_0) was 394.32 mg/L

Figure 5.12 Effect of pH of CHT derivatives solutions on chelation efficiency for Cu(II) ions

CHT was found to be more efficient in complex formation with Cu(II) ions at pH 5.5 as displayed in Table 5.22 and in Figure 5.12. Similar results were observed in case of TMCHT3 though poorer to CHT. Highly acidic pH for CHT and TMCHT, however, was discouraging. It is known that the attachment of Cu(II) ions with chitosan is possible through co-ordinate bonds by the donation of lone pair of electrons of amino, acetamido and hydroxyl groups. In highly acidic medium i.e. at pH 3.5 most of the amino groups are believed to be protonated and their involvement in such bond formation is less probable. In that case the scavenging of Cu (II) ions would be assigned to hydroxyl and N-acetyl groups. At slightly higher pH (pH 5.5), some fraction of amino groups remain unprotonated or free. The free amino groups, due to the presence of lone pair of electrons, are capable of forming coordinate linkages with copper ions and hence an enhanced chelation was observed at pH 5.5. Besides less availability of free amino groups due to quaternization and protonation in acidic reaction medium, TMCHT exert ionic repulsion to copper cations. The bulkier side methyl groups also act as barrier and lead to the decrease in chelation efficacy of trimethyl chitosan.

5.3.2.5 Effect of concentration of chitosan derivatives on chelation of Cu(II) ions

Similar to the study of chelation of calcium ions, the effect of concentration of different molecular weight chitosans on chelation of Cu (II) ions was investigated. The aqueous behaviour of chitosan in context to molecular weight and concentration and subsequent influence on chain conformation and viscosity is discussed in detail in chapter 2. These properties are expected to influence the metal binding capacity of chitosan. Since the concentration of chitosan in treatment bath was taken up to 2 g/L, accordingly a sufficiently higher initial concentration of Cu(II) ions i.e.754.95 mg/L in the solution was maintained. The pH of the reaction medium was adjusted to pH 5.5 using acetic acid. In order to understand chelation behaviour of chitosans, the effect of concentration of different molecular weights of chitosans for short (1h) and long duration (24 h) on the sorption of copper ions was studied. The residual concentration of Cu (II) ions in different chelating agents treated water, determined using equation 5.4, for 1h and 24 h is presented in Table 5.23 and Table 5.25. And the effect of concentration of chelating agents on chelation extent in terms of removal of Cu(II) ions from treated water, calculated using equation 5.6, is presented in Table 5.24 and Table 5.26 and graphically in Figure 5.13 and Figure 5.14.

Table 5.23 Residual Cu (II) ions present in treated water as a function of concentration of chelating agent for 1h treatment

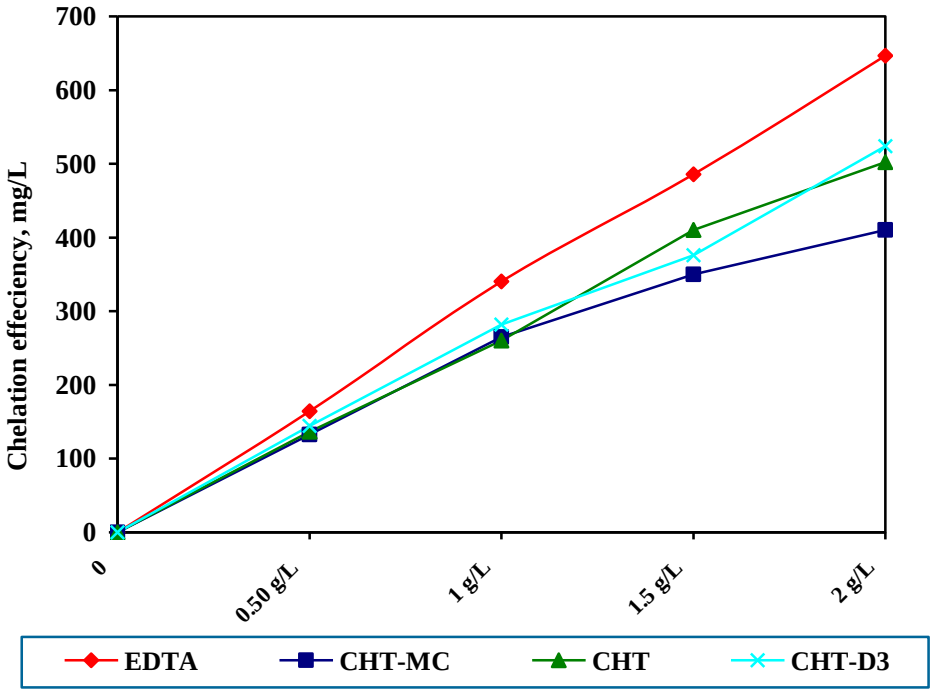
Conc, g/L	**Residual Cu(II) content (I_F, mg/L) in water treated with:**			
	Na_4EDTA	**CHT-MC**	**CHT**	**CHT-D3**
0.50	593.39	622.01	618.19	610.56
1.00	414.67	489.72	494.81	472.55
1.50	270.30	405.13	344.71	379.69
2.00	108.12	344.71	252.49	230.87

Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, CHT-D3=38,733;
Initial conc of Cu(II) ions (I_0)was 754.93mg/L, pH 5.5, Treatment time 1h

Table 5.24 Effect of concentration of chelating agents on chelation of Cu(II) ions for 1 h treatment

Conc, g/L	Cu(II) ions, mg/L, removed from water treated with:			
	Na_4EDTA	CHT-MC	CHT	CHT-D3
0.50	164.54 *(21.8)*	132.92 *(17.6)*	136.74 *(18.1)*	144.37 *(19.1)*
1.00	340.26 *(45.1)*	265.21 *(35.1)*	260.12 *(34.5)*	282.38 *(37.4)*
1.50	485.63 *(64.3)*	349.80 *(46.3)*	410.22 *(54.3)*	375.24 *(49.7)*
2.00	646.81 *(85.7)*	410.22 *(54.3)*	502.44 *(66.6)*	524.06 *(69.4)*

Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, CHT-D3=38,733;
Initial conc of Cu(II) ions (I_0) was 754.93mg/L, pH 5.5,
Values in parenthesis indicate chelation efficiency in terms of % removal



Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, CHT-D3=38,733;
Initial conc of Cu(II) ions (I_0) was 754.93mg/L, pH 5.5

Figure 5.13 Effect of concentration of chelating agents on chelation of Cu(II) ions for 1 h treatment

Table 5.25 Residual Cu (II) ions present in treated water as a function of concentration of chelating agent for 24h treatment

Conc, g/L	Residual Cu(II) content (I_F, mg/L) in water treated with:			
	Na_4EDTA	CHT-MC	CHT	CHT-D3
0.50	585.12	605.47	608.65	609.29
1.00	397.5	456.65	466.19	478.91
1.50	256.31	271.57	297.01	327.54
2.00	64.87	55.33	132.29	214.33

Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, CHT-D3=38,733; Initial conc of Cu(II) ions (I_0) was 754.93mg/L, pH 5.5

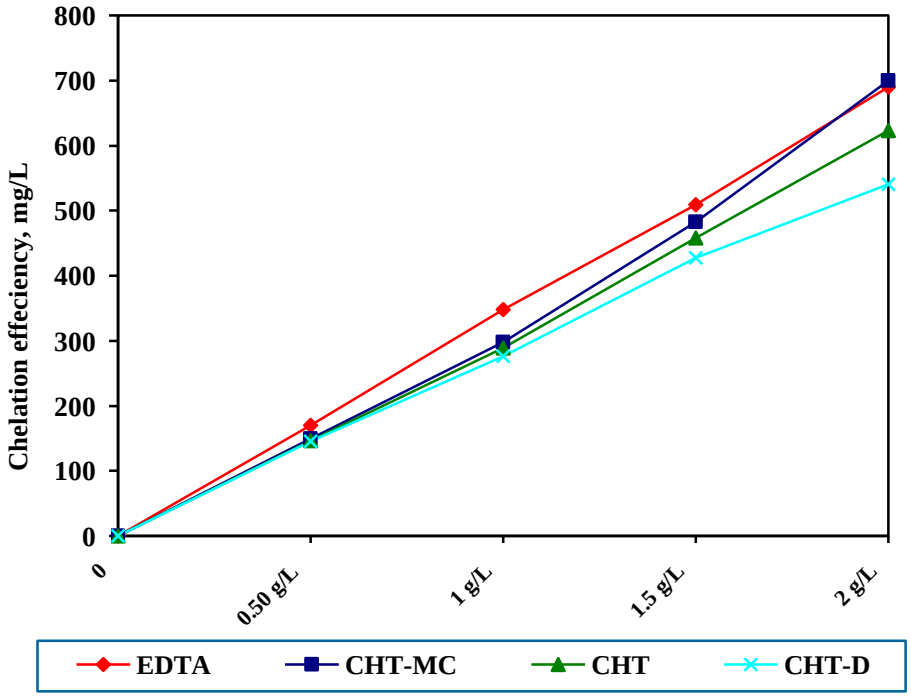
Table 5.26 Effect of concentration of chelating agents on chelation of Cu (II) ions for 24 h treatment

Conc, g/L	Cu(II) ions, mg/L, removed from water when treated with:			
	Na_2EDTA	CHT-MC	CHT	CHT-D3
0.50	169.81 *(22.5)*	149.46 *(19.8)*	146.28 *(19.4)*	145.64 *(19.3)*
1.00	357.43 *(47.3)*	298.28 *(39.5)*	288.74 *(38.3)*	276.02 *(36.6)*
1.50	498.62 *(66.1)*	483.36 *(64.0)*	457.92 *(60.7)*	427.39 *(56.6)*
2.00	690.06 *(91.4)*	699.60 *(92.7)*	622.64 *(82.5)*	540.60 *(71.6)*

Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, CHT-D3=38,73; Initial conc of Cu(II) ions (I_0) was754.93mg/L, pH 5.5, Values in parenthesis indicate chelation efficiency in terms of % removal

The behaviour of chitosan for sorption of copper ions was found to be very much similar to that observed with calcium ions except in the extent of adsorption. It was observed from Table 5.24 and Table 5.26 (Figure 5.13 and Figure 5.14) that the sorption curves for EDTA followed linearity with respect to concentration and almost same level of chelation efficacy observed for both the durations of treatment. The amount of Cu(II) ions removed from treated liquor was found to be increased with increase in concentration of chitosan derivatives. The chelation behaviour of chitosan derivatives in context to concentration for different molecular weights, however, was observed to be anomalous when examined at different durations of treatment. In first hour of treatment or for short treatment of time as depicted in Figure 5.14, the sorption curve for low molecular weight chitosan (CHT-D3) followed almost linearity in given concentration range, while high molecular weight chitosans showed some deviations at higher

concentrations. The curves for CHT and CHT-MC were found slightly declined down ward when concentration reached to 2 g/L and was more prominent for CHT-MC.



Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, CHT-D3=38,733; Initial conc of Cu(II) ions (I_0) was754.93mg/L, pH 5.5

Figure 5.14 Effect of concentration of chelating agents on chelation of Cu(II) ions for 24h treatment

Further, it was observed that the extent of chelation was maximum for low molecular weight chitosan when treated for short time and decreased with increase in molecular weight i.e. in the order of CHT-D3>CHT>CHT-MC. On prolong treatment i.e. when the treatment was extended to 24 h, as demonstrated in Figure 5.15, the chelation behaviour of chitosan was significantly altered particularly for high molecular weight chitosans. The sorption behaviour of low molecular weight chitosan (CHT-D3) was not much influenced except slight improvement in it but behaviour was entirely changed when the molecular weight was increased. A slightly upward trend in sorption of metal ions from waster was noticed when the concentrations of high molecular weight chitosans were increased. The order in degree of sorption by chitosan with respect to molecular weight was, however, reversed as against short duration of treatment. The extent of sorption of

copper ions now increased with increase in molecular weight i.e. in the order of CHT-MC>CHT>CHT-D3.

Low molecular weight chitosans (CHT-D3) in solution are probably more open and extended due to less intra and intermolecular forces and thus provide more surface area for chelation reactions and therefore shows enhanced sorption. High molecular weight chitosan (CHT-MC) molecules in solution, on the other hand, are more complex due to overlapping of macromolecules and therefore provide fewer sites for interaction resulting in to decreased sorption. On prolong treatment, high molecular weight chitosans may under go depolymerization due to hydrolysis and also may display more opened conformation due to disentanglement leading to uncovering of more sites for chelation [50, 51]. In all cases, increase in concentration obviously leads to increased sites and the chelation extent. Studies related to viscosity behaviour in chapter 2 revealed that the high molecular weight chitosans, during the short duration of treatments, are still in aggregated state due to entanglement and overlapping at increased concentration may contribute to declined chelation. Enhanced chelation for CHT-MC at 2 g/L concentration may also be ascribed to the presence of more number of free amino groups (less protonation) due to relatively lower chitosan to acetic acid ratio.

5.3.2.6 Effect of particle size chelation of Cu(II) ions

The reduction in particle size of chitosan macromolecule to nano level can furnish increased surface area and increased accessibility of reactive sites (ligands) for metal binding. A detailed study on synthesis and various properties and applications of nano chitosan (CHTN) dispersion is discussed in detail in chapter 3. In brief; the ionotropic gelation technique of chitosan with sodium tripolyphosphate (TPP) was employed for the synthesis of nano chitosan dispersions. The varying levels of particle size of nano chitosan, for a given molecular weight chitosan, were obtained by changing the concentration of polymer (chitosan). Two different nano chitosans of average particle sizes 408.73 nm and 534.2 nm, considered for present experiment, were obtained from CHT at concentrations 1.5 g/L and 2 g/L respectively. These stocks solutions were employed for chelation study of copper ions at concentration 1g/L, obtained by dilution.

Table 5.27 Residual Cu(II) content in chitosan treated of varying particle size

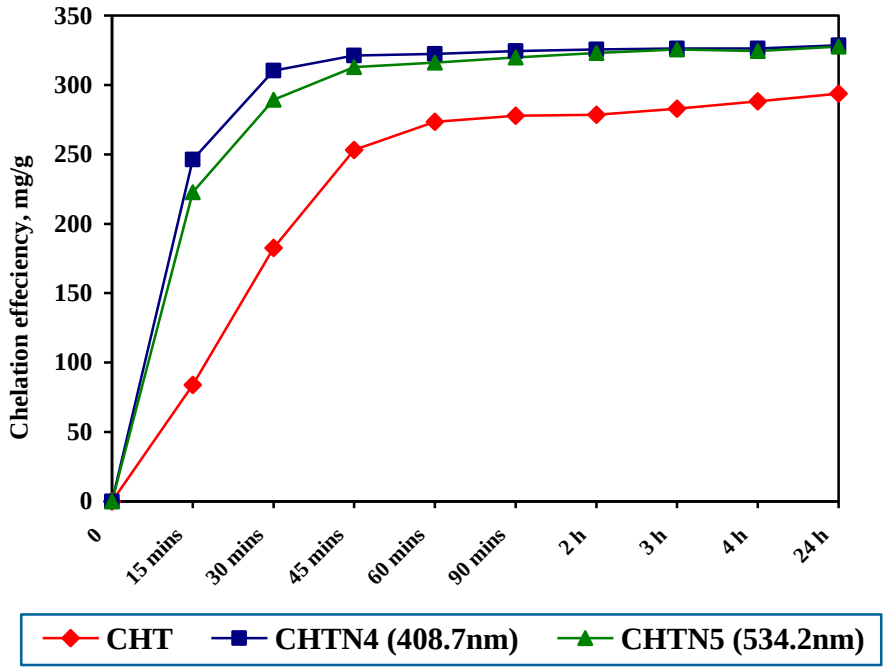
Treatment time	Residual Cu (II) ions content in water (I_F, mg/L) treated with:		
	CHT (Particle size 4014 nm)	**CHTN4 (Particle size 408.73nm)**	**CHTN5 (Particle size 534.2nm)**
15 min	310.37	148.19	171.72
30 min	211.79	83.95	104.94
45 min	141.19	73.14	81.41
60 min	120.84	71.88	78.23
90 min	116.39	69.96	74.41
2 h	115.75	68.69	71.23
3 h	111.30	68.5	68.69
4 h	106.21	68.5	69.96
24 h	100.49	65.51	66.78

Initial concentration of Cu(II) ions (I_0) was 394.32 mg/L, pH 5.5, Concentration of chelating agent 1g/L

Table 5.28 Effect of particle size of chitosan on extent chelation of Cu (II) ions

Treatment time	Chelated Ca^{+2} ions (mg/g) from water treated with:		
	CHT (Particle size 4014 nm)	**CHTN4 (Particle size 408.73nm)**	**CHTN5 (Particle size 534.2nm)**
15 min	83.95	246.13	222.60
30 min	182.53	310.37	289.38
45 min	253.13	321.18	312.91
60 min	273.48	322.44	316.09
90 min	277.93	324.36	319.91
2 h	278.57	325.63	323.09
3 h	283.02	326.27	325.63
4 h	288.11	326.27	324.36
24 h	293.83	328.81	327.54

Initial conc of Cu(II) ions (I_0) was 394.32 mg/L, pH 5.5, Conc of chelating agent 1g/L



Conc of chelating agent 1g/L

Figure 5.15 Effect of particle size of chitosan on extent of chelation Cu(II) ions

The residual Cu(II) ions content in treated water, determined using equation 5.4, are presented in Table 5.27. The effect of particle size on the chelation efficiency of chitosan is shown in Table 5.28 and graphically in Figure 5.15. The results revealed that the rate of chelation enhanced by the reduction in particle size of chitosan indication the faster establishment of equilibrium. Further, the absolute chelation value at equilibrium was found to be increased. Besides the increased surface area, the added phosphorous (P) of TPP can also act as a ligands for scavenging the copper ions [49].

5.3.3 Decolourization of dye waste water

Textile wet processing operations produce high volumes of effluent waste water of varied composition, often containing electrolytes plus organic surfactants, solvents and dyes. The amount of colourants present in textile effluents is usually very small; however, these are highly detectable and have become a pollution concern for several reasons. Dyes are highly dispersible aesthetic pollutant which may contribute aquatic toxicity. Some of azo dyes are mutagenic and carcinogenic. These colorants are difficult to treat and interfere with UV light disinfection operations [3, 11, 24]. Several difficulties

are encountered in removal of dyes from waste water. By design, dyes are highly stable molecules, made to resist degradation by light, chemical, biological and other exposures. Commercial dyes are usually mixtures of large complex and vary widely in chemical constitutions and properties. Further, dyeing waste water includes other materials such as electrolytes, dyeing assistants, surfactants, acids/alkalies etc [3, 6, 24, 57].

The best way to control colour pollution is the good source reduction, based on administrative and engineering controls, process and product design, and work practices. Source reduction techniques result in higher efficiency, improved productivity, and lower cost and less colour**.** However, quantitative dyebath exhaustion is not possible with most systems. Equilibrium is established in dyeing and washing off that always leave some amount dye in the waste water. In commercial process, that may be from almost none to over 50% of the total dye [1, 4, 24]. Improving fibre reactive dye fixation efficiency, developments of high exhaustive dyes (HE series) in reactive dyes [6], substrate modification, e.g. cationization of cellulose, for improved exhaustion [58] etc can result into minimum wash off. Cotton fabric pretreated with chitosan and its quaternized derivatives have found to improve the exhaustion substantially as discussed in chapters 2 and 4 respectively. Scaling down the particle size of chitosan to nano level and its pretreatment to cotton fabric was found to leave the wash almost colourless, as demonstrated in chapter 3. Such treatments definitely reduce the pollution load.

In addition to source reduction methods and improving the dyeing efficiencies, handling, house keeping and cleanup, there are also waste water decolourization treatment strategies. Most current practices fall into two main classes: those that destroy or modify the offending coloured species and those that physically remove the coloured species [24]. Some of the important methods are [11, 23, 59, 60]:

- Chemical (ozone, activated peroxide, chlorine, chlorine dioxide, electrolysis etc) or biological decolourization to destroy dyes, which can leave harmful organic residues and sludges. Large amount of dyes belong to azo class. Decolorization of azo dyes normally begins with initial reduction or cleavage of azo bond anearobically, which results into colorless compounds. This is followed by complete degradation of aromatic amines strictly under aerobic conditions. Microorganisms capable of degrading azo dyes include *proteus*

spp, *Enterococcus spp* , *Streptococcus spp*, *Bacillus cereus*, *Streptomyces spp* etc;

- Removal by precipitation, ion exchange and sorption, which result in the solid waste disposal. Coagulation and flocculation either with inorganic, inorganic/organic or organic systems have the advantage of reducing COD and BOD. They are generally cheap to operate but low capacity to remove dyes. Adsorption systems have the ability to remove dyes and other contaminants from aqueous systems as complete molecules, thereby substantially reducing the contaminant load. Examples of popular adsorbents are activated carbon, inorganic adsorbents such as brown coal, clays etc, and biological adsorbents such as chitin, chitosan, fungal biomass, bacterial biomass, rice hull, sugarcane bagasse etc. These products are naturally abundant and cheap;
- Recycling of process waters directly or after some treatment to remove and reclaim salts and processing agents. Reverse osmosis can give water of excellent quality. However membrane techniques donot immobilize the contamination on to a solid substrate; instead, they concentrate it as a liquid. Further, they are more suitable for reducing TDS rather than dyes.

The multitude of commercial dyes and dyeing systems makes it highly unlikely that any one single method will alone meet the demands of every situation, each having its own set of specific problems depending on the dyeing system, chemical use and procedures. Often combination, mostly in multi stage, of above enumerated methods can give satisfactory results.

Recently the possibilities of adsorption processes to remove dyestuffs discharged from textile industries have been concerned in great extent, since these would have potential advantage of allowing recovery of dyestuffs in concentrated form. Many common sorbents have ionic interactions like polyelectrolytes, or a highly porous structure as found in activated carbon with extremely high surface area which is ideal for sorption. Conventionally, activated charcoal is employed a sorbent for the decolourization effluent after the ion exchange process i.e. at the final stage of effluent treatment. Laboratory work has shown that dye solutions can be rendered colourless with

carbon alone, but that the binding capacity is rather low-even in solutions where dye is the only contaminant. Also, carbon is a wide spectrum adsorbent and, consequently, its dye binding capacity is further lowered by the presence of much larger amounts of organic contaminant [24, 59]. Among the oldest methods of treatment of waste water is the use of adsorbents from biological matter or biomass [23].

Sorption is influenced by many physico chemical factors such as dye-sorbent interaction, sorbent surface area, temperature, pH, contact time, sorbent concentration etc. The nature, size and shape of the sorbent particles determine the manner of use (i.e. batch reactor/ clarifier Vs continuous/filter) based on contact times, sorption rates, settling times etc [3, 6, 24]. Due to unique molecular structure, chitosan has extremely high affinity for many classes of dyes including disperse, direct, reactive, acid, vat, sulphur and naphthols. Rate of diffusion of dyes of chitosan is similar to cellulose [24, 61, 62]. The sorption capacity of chitosan has been reported to be affected with increase in molecular weight of dyes [24, 63]. According to theory of dyeing the sorption of dyes by chitosan is also exothermic, an increase in temperature leads to an increase in sorption rate but decrease in sorption capacity and followed the simple and semi empirical Langmuir and Freundlich isotherms [3, 24, 64]. At low concentrations, dye uptake conforms well to Langmuir isotherm model as a result of definite number of amino groups.

The present investigation aims at partly to deal with the problems of dye house waste water decolorisation using chitosan of varying molecular weight and its trimethyl chitosan chloride derivative as sorbents. In order to understand the sorption behaviour of chitosan, two different grades namely CHT-MC and CHT having molecular weights 654,127 and 135,839 respectively having similar DAC values of 90% were chosen. Attributing to the presence of permanently positive charge on polymer backbone, a quaternized derivative i.e. trimethyl chitosan chloride (TMCHT3) with degree of quaternization 51% was also taken for the investigation. The sorption study on chitosan derivatives was conducted separately for effluent water containing anionic dyes namely C. I. Direct Red 81(mol wt. 675.6) and C. I. Acid Blue 158 (mol.wt.468). Two different protocols were followed to conduct the experiment. In one, the sorbent at neutral pH was treated with dye effluent containing known amount of purified dye (25 mg/L).After

specified dwell time for reaction, the mixture was filtered and the filtrate analysed for dye content spectrometrically. Since TMCHT3 was soluble at neutral pH, it was recovered by alkali treatment. In another route, predissolved chitosan at acidic pH was used for treatment with dye effluent. After the specified treatment time, the mixture was neutralized with sodium hydroxide solution to recover chitosan and the aliquot obtained after filtration was analysed for dye content. The amount of dye remained in treated liquors were determined form calibration curve of absorbance (optical density) against concentration according to Beer-Lamberts' law. The absorbance (O.D.) values of dye solutions measured for different concentrations at maximum wave length (λ_{max}) is presented graphically in Figure 5.16.

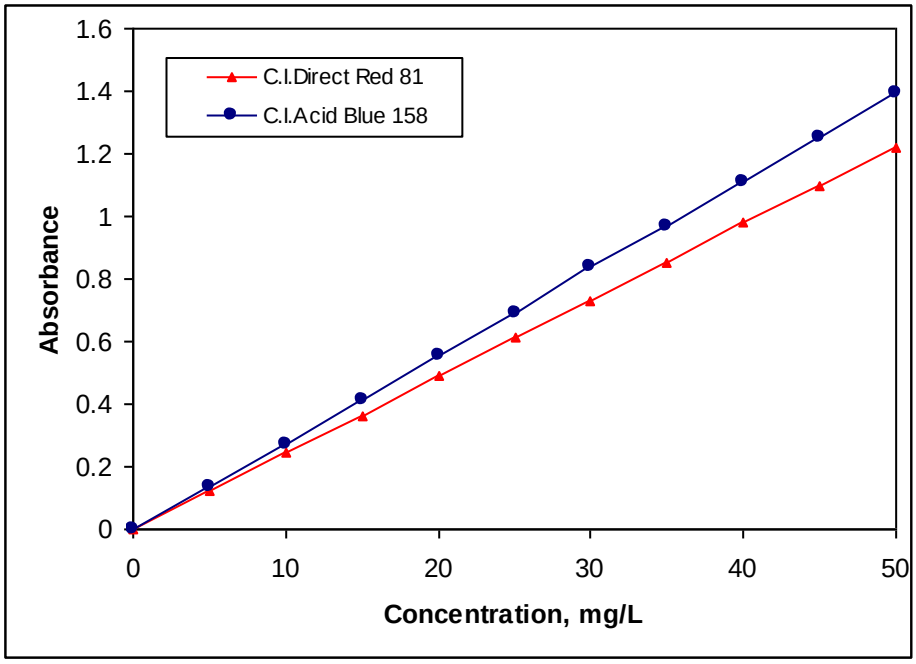


Figure 5.16 Calibration curves for dye solutions

Dye waste water (effluent) treatment with chitosan at neutral pH is heterogeneous where as treatment with quaternized derivative of chitosan (TMCHT3) is homogeneous, since it is water soluble at neutral pH. The examination of amount of dye remained in treated liquor, by optical density method, is illustrated in Table 5.29 and Table 5.31 for C. I. Direct Red 81 and C. I. Acid Blue 158 respectively. The sorption kinetics of chitosan

and TMCHT3 for direct and acid dyes at neutral pH is presented in Table 5.30 and Table 5.32 and graphically in Figure 5.17 and Figure 5.18 respectively.

Table 5.29 Residual C. I. Direct Red 81 content in effluent treated with different adsorbents at neutral pH

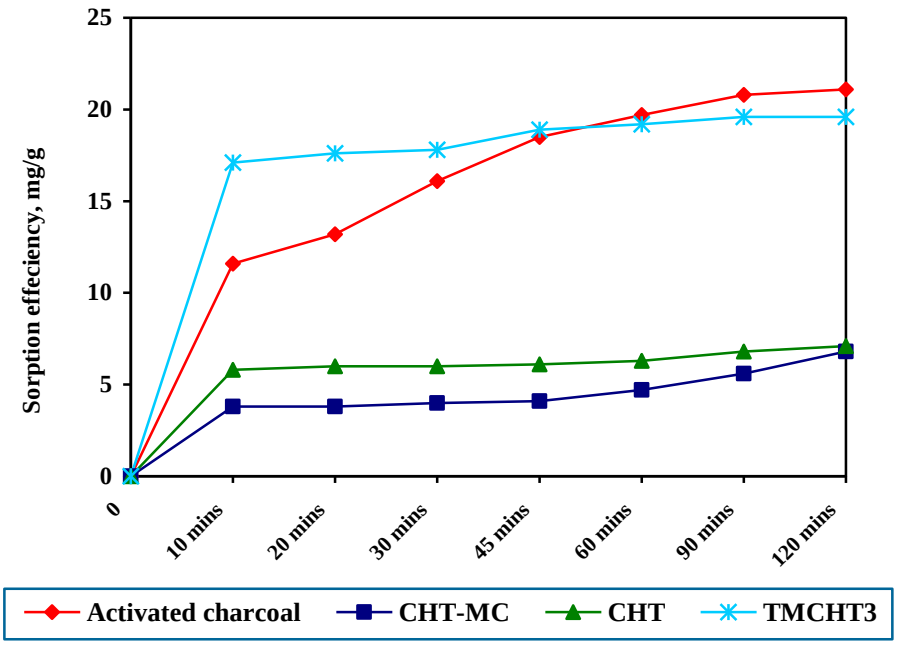
Treatment time, min	Activated charcoal		CHT-MC		CHT		TMCHT3	
	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L
10	0.338	13.4	0.516	21.2	0.462	19.2	0.190	7.9
20	0.291	11.8	0.516	21.2	0.460	19.0	0.185	7.4
30	0.228	8.9	0.515	21.0	0.460	19.0	0.182	7.2
45	0.162	6.5	0.500	20.9	0.455	18.9	0.140	6.1
60	0.125	5.3	0.495	20.3	0.453	18.7	0.129	5.8
90	0.100	4.2	0.480	19.4	0.450	18.2	0.127	5.4
120	0.095	3.9	0.430	18.2	0440	17.9	0.127	5.4

Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, DQ: TMCHT3= 50.92%; Conc of adsorbent 1 g/L, pH 7, Initial conc of dye was (I_0) 25 mg/L with corresponding O.D. 0.613 at λ_{max} 510nm

Table 5.30 Sorption kinetics of C.I.Direct Red 81 at neutral pH

Treatment time, min	Adsorbed C. I. Direct Red 81 (mg/g) from effluent treated with:			
	Activated charcoal	CHT-MC	CHT	TMCHT3
10	11.6 *[46]*	3.8 *[15]*	5.8 *[23]*	17.1 *[68]*
20	13.2 *[53]*	3.8 *[15]*	6.0 *[24]*	17.6 *[70]*
30	16.1 *[64]*	4.0 *[16]*	6.0 *[24]*	17.8 *[71]*
45	18.5 *[74]*	4.1 *[16]*	6.1 *[24]*	18.9 *[77]*
60	19.7 *[79]*	4.7 *[19]*	6.3 *[25]*	19.2 *[77]*
90	20.8 *[83]*	5.6 *[22]*	6.8 *[27]*	19.6 *[78]*
120	21.1 *[84]*	6.8 *[27]*	7.1 *[28]*	19.6 *[78]*

Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; DQ: TMCHT3= 50.92%; Conc of adsorbent 1 g/L, Initial conc of dye (I_0) was 25 mg/L, pH 7, Values in bracket indicate the % sorption of dye



Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; DQ: TMCHT3= 50.92%; Conc of adsorbent 1 g/L, Initial conc of dye (I_0) was 25 mg/L, pH 7

Figure 5.17 Sorption kinetics of C.I.Direct Red 81 at neutral pH

Results reveal the satisfactory sorption efficiency of TMCHT3 and comparable with activated charcoal. TMCHT3 attained the sorption equilibrium in 30 minutes and was little influenced or remained almost stable when the treatment was extended. The sorption ability of CHT and CHT-MC, however, at neutral pH was not found to be satisfactory. Low molecular weight chitosan i.e. CHT showed somewhat higher capacity than that of CHT-MC. The sorption dye of latter was extremely slow. The higher sorption ability of quaternized derivative may be attributed to the presence of permanent cationic groups that form ionic linkages with anionic groups on dyes. Saturation in adsorption by TMCHT may be the indication of presence of definite number of dye sites. Poor adsorption by parent chitosan may be the presence of insoluble chitosan aggregates in treatment bath. The insoluble aggregates provide very small surface area for the interaction with dyes and also the diffusion of dye into macromolecular structure is precluded due to compact structure.

Table 5.31 Residual C. I. Acid Blue 158 content in effluent treated with different adsorbents at neutral pH

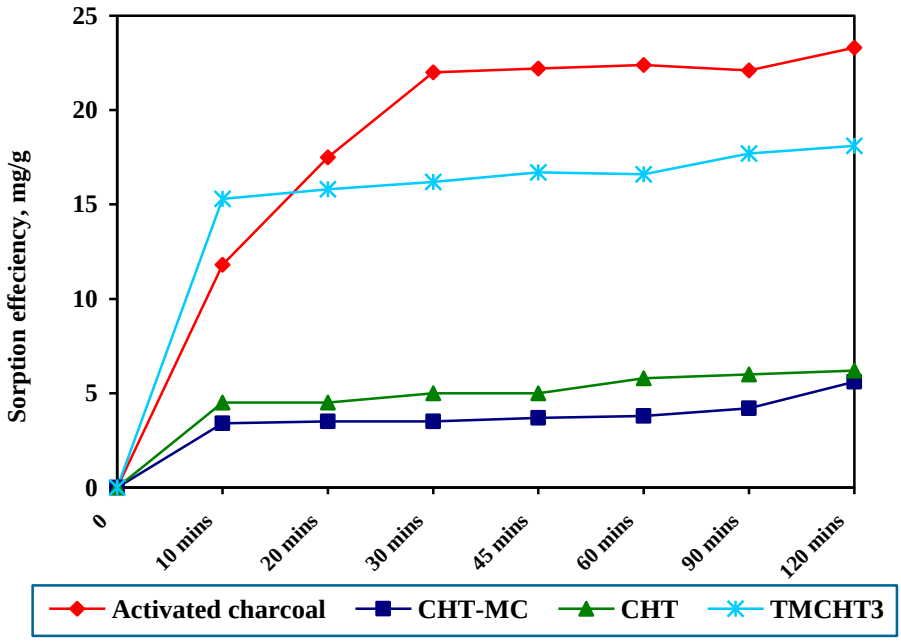
Treatment time, Min	Activated charcoal		CHT-MC		CHT		TMCHT3	
	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L
10	0.355	13.2	0.595	21.6	0.560	20.5	0.260	9.7
20	0.205	7.5	0.589	21.5	0.560	20.5	0.245	9.2
30	0.070	3.0	0.589	21.5	0.550	20.0	0.240	8.8
45	0.065	2.8	0.585	21.3	0.550	20.0	0.230	8.3
60	0.060	2.6	0.580	21.2	0.538	19.2	0.232	8.4
90	0.068	2.9	0.560	20.8	0.520	19.0	0.195	7.3
120	0.040	1.7	0.540	19.4	0.518	18.8	0.190	6.9

Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; DQ: TMCHT3= 50.92%;
Conc of adsorbent 1 g/L, Initial conc of dye (I_0) was 25 mg/L with corresponding O.D. 0.690 at λ_{max} 620nm

Table 5.32 Sorption kinetics of C.I.Acid Blue158 at neutral pH

Treatment time, min	Adsorbed C.I. Acid Blue158 (mg/g) from effluent treated with:			
	Activated charcoal	CHT-MC	CHT	TMCHT3
10	11.8 *[47]*	3.4 *[14]*	4.5 *[18]*	15.3 *[61]*
20	17.5 *[70]*	3.5 *[14]*	4.5 *[18]*	15.8 *[63]*
30	22.0 *[80]*	3.5 *[14]*	5.0 *[20]*	16.2 *[65]*
45	22.2 *[89]*	3.7 *[15]*	5.0 *[20]*	16.7 *[67]*
60	22.4 *[90]*	3.8 *[15]*	5.8 *[23]*	16.6 *[66]*
90	22.1 *[88]*	4.2 *[17]*	6.0 *[24]*	17.7 *[71]*
120	23.3 *[93]*	5.6 *[22]*	6.2 *[25]*	18.1 *[72]*

Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; DQ: TMCHT3= 50.92%,
Conc of adsorbent 1 g/L, Initial conc of dye (I_0) was 25 mg/L, pH 7, Values in brackets indicate the % sorption of dye



Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, DQ: TMCHT3=50.92%; Conc of adsorbent 1 g/L, Initial conc of dye (I_0) was 25 mg/L, pH 7

Figure 5.18 Sorption kinetics of C.I.Acid Blue158 at neutral pH

One way to enhance the diffusion of dye into chitosan particles, a pretreatment with swelling agent to the latter may be given. Highly polar solvent such as *N*-methyl-2-pyrrolidone (NMP) may be employed which is often used as a swelling agent during quaternization reactions [48, 65]. This solvent can swell and open up the chitosan particles and facilitate the greater penetration of dyes. Chitosan was treated with NMP for 24h and rinsed before used sorption of dyes. The preswollen chitosan (NMP-CHT) showed improved sorption for direct and acid dyes, nevertheless longer time consumed, can be observed from Table 5.33 and Table 5.34 and Figure 5.19.

Table 5.33 Effect of NMP pretreatment on adsorption efficiency chitosan for direct and acid dyes at neutral pH

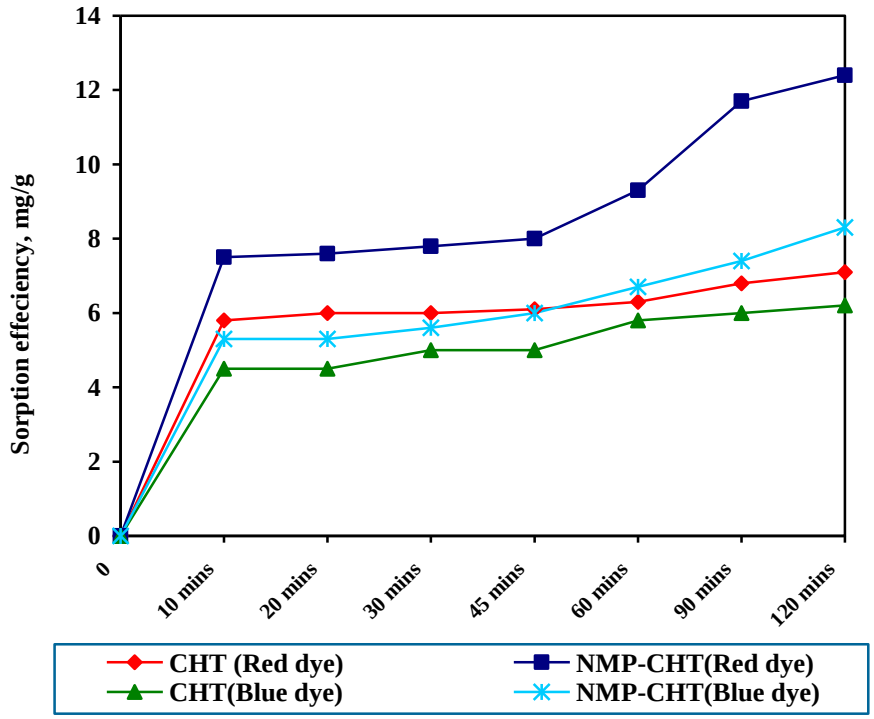
Treatment time, min	C.I.Direct Red 81				C.I.Aicd Blue158			
	CHT treated effluent		CHT-NMP treated effluent		CHT treated effluent		CHT-NMP treated effluent	
	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L
10	0.462	19.2	0.435	17.5	0.560	20.5	0.545	19.7
20	0.460	19.0	0.430	17.4	0.560	20.5	0.545	19.7
30	0.460	19.0	0.420	17.2	0.550	20.0	0.540	19.4
45	0.455	18.9	0.415	17.0	0.550	20.0	0.520	19.0
60	0.453	18.7	0.380	15.7	0.538	19.2	0.500	18.3
90	0.450	18.2	0.325	13.3	0.520	19.0	0.485	17.6
120	0440	17.9	0.305	12.6	0.518	18.8	0.450	16.7

Conc of adsorbent 1g/L, Initial conc of dye (I_0) was 25 mg/L

Table 5.34 Effect of NMP pretreatment on sorption ability of CHT for direct and acid dyes at neutral pH

Treatment time, min	Amount of dye adsorbed, mg/g			
	C.I.Direct Red 81		C.I.Aicd Blue158	
	CHT treated effluent	NMP-CHT treated effluent	CHT treated effluent	NMP-CHT treated effluent
10	5.8 *[23]*	7.5 *[23]*	4.5 *[18]*	5.3 *[21]*
20	6.0 *[24]*	7.6 *[30]*	4.5 *[18]*	5.3 *[21]*
30	6.0 *[24]*	7.8 *[31]*	5.0 *[20]*	5.6 *[22]*
45	6.1 *[24]*	8.0 *[32]*	5.0 *[20]*	6.0 *[24]*
60	6.3 *[25]*	9.3 *[37]*	5.8 *[23]*	6.7 *[27]*
90	6.8 *[27]*	11.7 *[47]*	6.0 *[24]*	7.4 *[30]*
120	7.1 *[28]*	12.4 *[50]*	6.2 *[25]*	8.3 *[33]*

Conc of adsorbent 1 g/L, Initial conc of dye (I_0) 25 mg/L, pH 7; CHT-NMP is CHT pretreated with NMP; Values in brackets indicate the % sorption of dye



Conc of adsorbent 1 g/L, Initial conc of dye 25 mg/L, pH 7, CHT-NMP is CHT pretreated with NMP

Figure 5.19 Effect of NMP pretreatment on sorption ability of CHT direct and acid dyes at neutral pH

In two phase method, the adsorption stage performed is homogeneous i.e. chitosan is dissolved in acidic medium for the interaction with dye anions followed by precipitation for the recovery of chitosan-dye complex. The residual dye in aliquot, determined by optical density method, respectively for C.I.Direct Red 81 and C.I.Acid Blue158 is given in Table 5.35 and Table 5.38. The sorption kinetics of these dyes on chitosan derivatives presented in these tables and corresponding graphically in Figure 5.20 and Figure 5.21 was encouraging. All the chitosan derivatives namely CHT, CHT-MC and TMCHT3 showed almost similar level of adsorption and higher than conventional activated charcoal. The equilibrium was reached within 30 minutes and then after very little sorption notices. The sorption efficiency THCHT3 in acidic pH was found to be enhanced than at neutral pH. In all cases, the sorption of direct dyes was higher than that of acid dyes however the rate of adsorption of acid dyes was some what faster than direct dyes. In acidic pH, most of the amino groups on chitosan are protonated and positively charged to form ionic linkages with anionic groups on dyes. Further, in

dissolved state the chitosan macromolecules are extended and furnish larger number of accessible positive sites for dye attachment. Unquaternized or free amino groups in quaternized chitosan also get protonated becoming additional dye sites. The molecular weight of C.I.Acid Blue 158 (Mol wt 495.45) is lesser than C.I.Direct Red 81 (Mol wt. 675.6) has higher mobility and may be responsible faster kinetics but the attachment is solely ionic. Direct dye on the other hand exhibits long, linear and planar structure and is retained on glucosamine residues, in addition to ionic linkages, by H-bonding and secondary valance forces analogous to the interaction of cellulose with direct dyes [66]. Therefore, higher sorption of direct dye than acid dye on chitosan macromolecules is seen. The final appearance of various chitosan derivatives treated coloured waste water is shown in Figure 5.22 and Figure 5.23.

Table 5.35 Residual C. I. Direct Red 81 content in effluent treated with different adsorbents at acidic pH

Treatment time, min	**Activated charcoal**		**CHT-MC**		**CHT**		**TMCHT3**	
	O.D.	**Dye content (I_F), mg/L**	**O.D.**	**Dye content (I_F), mg/L**	**O.D.**	**Dye content (I_F), mg/L**	**O.D.**	**Dye content (I_F), mg/L**
10	0.338	13.4	0.255	10.7	0.230	9.6	0.227	8.8
20	0.291	11.8	0.128	5.7	0.125	5.2	0.120	4.9
30	0.228	8.9	0.067	3.0	0.064	2.7	0.084	3.5
45	0.162	6.5	0.045	2.0	0.060	2.6	0.068	3.1
60	0.125	5.3	0.050	2.1	0.066	2.9	0.069	3.2
90	0.100	4.2	0.045	2.0	0.065	2.8	0.067	3.0
120	0.095	3.9	0.025	1.8	0.067	3.0	0.069	3.2

Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, DQ: TMCHT3= 50.92%;
Conc of adsorbent 1 g/L, pH 3.5, Initial conc of dye was (I_0) 25 mg/L with corresponding O.D. 0.613 at λ_{max} 510nm

Table 5.36 Sorption kinetics of C.I.Direct Red 81 at acidic pH

Treatment time, min	Adsorbed C. I. Direct Red 81 (mg/g) from effluent treated with:			
	Activated charcoal	CHT-MC	CHT	TMCHT3
10	11.6 *[46]*	14.3 *[54]*	15.4 *[62]*	16.2 *[65]*
20	13.2 *[53]*	19.3 *[77]*	19.8 *[79]*	20.1 *[80]*
30	16.1 *[64]*	22.0 *[88]*	22.3 *[89]*	21.5 *[84]*
45	18.5 *[74]*	23.0 *[92]*	22.4 *[90]*	21.9 *[88]*
60	19.7 *[79]*	22.9 *[92]*	22.1 *[88]*	21.8 *[87]*
90	20.8 *[83]*	23.0 *[92]*	22.2 *[89]*	22.0 *[88]*
120	21.1 *[84]*	23.2 *[93]*	22.0 *[88]*	21.8 *[87]*

Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; DQ: TMCHT3= 50.92%;
Conc of adsorbent 1 g/L, Initial conc of dye (I_0) was 25 mg/L, pH 3.5; Values in bracket indicate the % sorption of dye

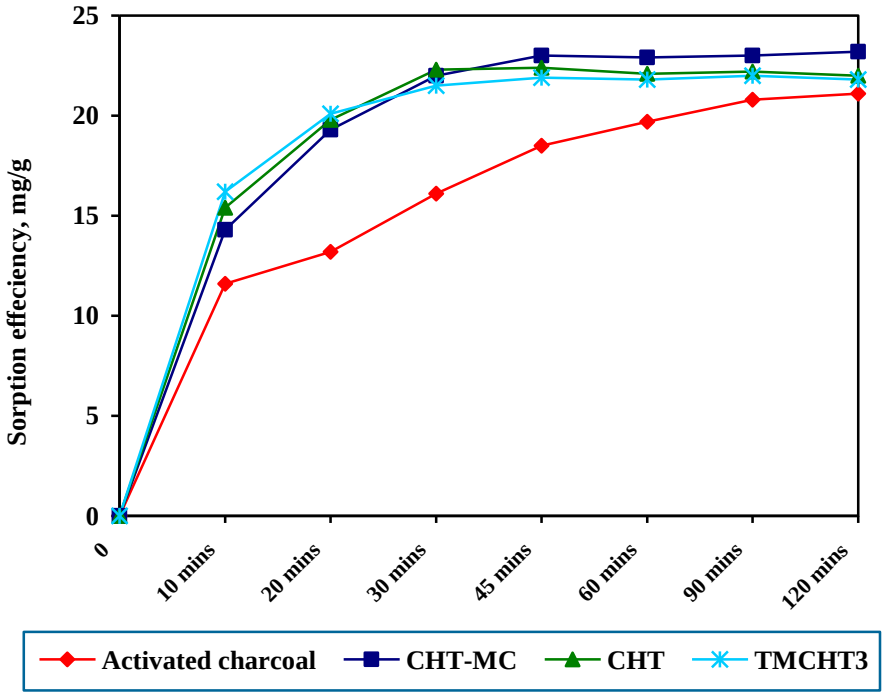


Figure 5.20 Sorption kinetics of C.I.Direct Red 81 at acidic pH

Table 5.37 Residual C. I. Acid Blue158 content in effluent treated with different adsorbents at acidic pH

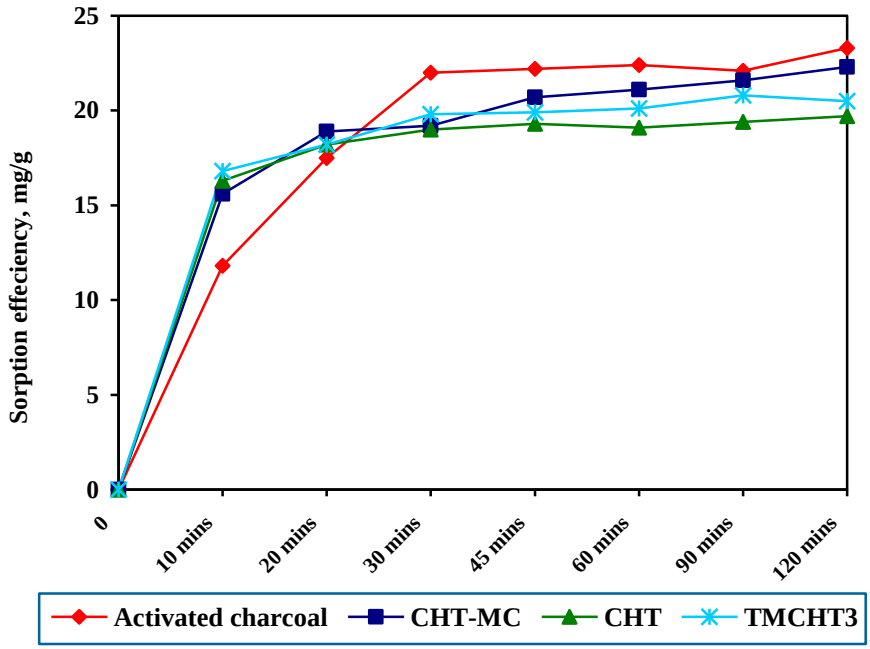
Treatment time, min	Activated charcoal		CHT-MC		CHT		TMCHT3	
	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L
10	0.355	13.2	0.260	9.4	0.230	8.3	0.225	8.2
20	0.205	7.5	0.160	6.1	0.190	6.8	0.190	6.8
30	0.070	3.0	0.169	6.0	0.168	6.0	0.138	5.2
45	0.065	2.8	0.120	4.3	0.155	5.7	0.137	5.1
60	0.060	2.6	0.100	3.9	0.165	5.9	0.132	4.9
90	0.068	2.9	0.090	3.4	0.145	5.6	0.115	4.2
120	0.040	1.7	0.062	2.7	0.140	5.3	0.125	4.5

Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; DQ: TMCHT3= 50.92%;
Conc of adsorbent 1 g/L, pH 3.5; Initial conc of dye (I_0) was 25 mg/L with corresponding O.D. 0.690 at λ_{max} 620nm

Table 5.38 Sorption kinetics of C.I.Acid Blue158 at acidic pH

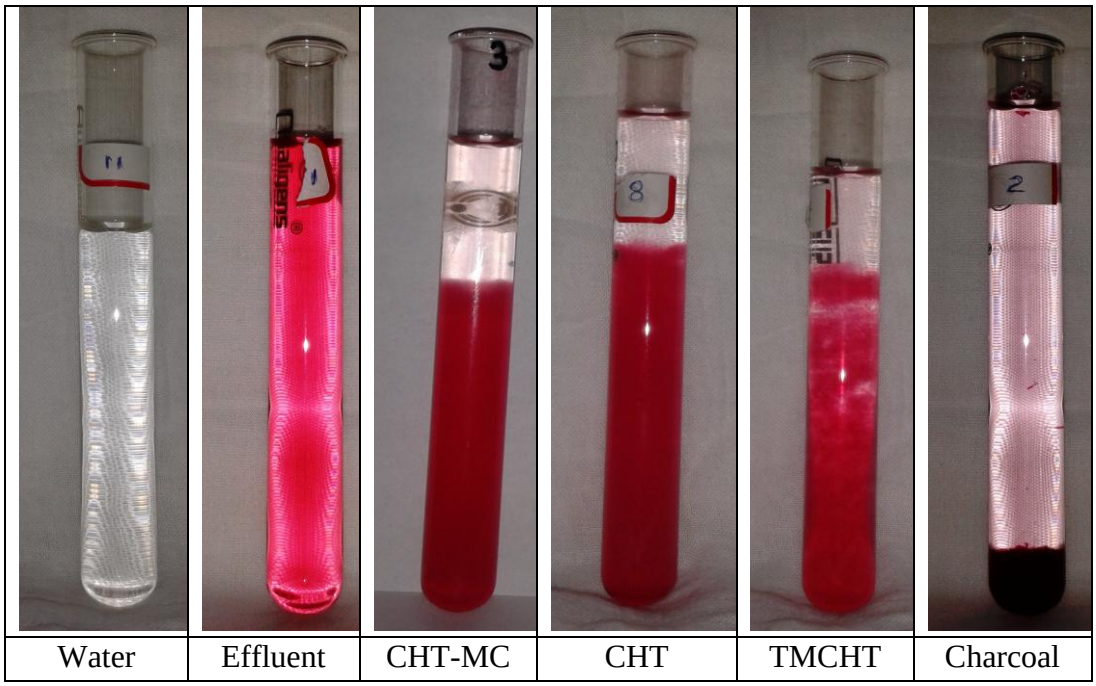
Treatment time, min	Adsorbed C.I. Acid Blue158 (mg/g) from effluent treated with:			
	Activated charcoal	CHT-MC	CHT	TMCHT3
10	11.8 *[47]*	15.6 *[62]*	16.3 *[65]*	16.8 *[67]*
20	17.5 *[70]*	18.9 *[76]*	18.2 *[73]*	18.2 *[73]*
30	22.0 *[80]*	19.2 *[77]*	19.0 *[77]*	19.8 *[79]*
45	22.2 *[89]*	20.7 *[83]*	19.3 *[72]*	19.9 *[80]*
60	22.4 *[90]*	21.1 *[84]*	19.1 *[76]*	20.1 *[80]*
90	22.1 *[88]*	21.6 *[86]*	19.4 *[78]*	20.8 *[83]*
120	23.3 *[93]*	22.3 *[92]*	19.7 *[79]*	20.5 *[82]*

Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; DQ: TMCHT3= 50.92%;
Conc of adsorbent 1 g/L, Initial conc of dye (I_0) was 25 mg/L, pH 3.5; Values in brackets indicate the % sorption of dye



Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; DQ: TMCHT3= 50.92%; Conc of adsorbent 1 g/L, Initial conc of dye (I_0) was 25 mg/L, pH 3.5

Figure 5.21 Sorption kinetics of C.I.Acid Blue158 at acidic pH



Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; DQ: TMCHT3= 50.92%

Figure 5.22 Effluents containing C. I. Direct Red 81 treated various adsorbents

Water	Effluent	CHT-MC	CHT	Charcoal

Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; DQ: TMCHT3= 50.92%

Figure 5.23 Effluents containing C. I. Acid Blue 158 treated various adsorbents

REFERENCES

1. N. Manivasakam, *Water used in textile processing-quality, treatment and analysis* (1995) Sakthi Publications, Coimbatore

2. Anju Singh, Richa Gautam and Rajan Sharma, "Performance evaluations of a common effluent treatment plant (CETP) treating textile wastewaters in India", *Journal of Industrial Pollution Control*, **24** (2), (2008) 111-121

3. P. K. Dutta, K. Durgabhavani and S. Naveen, "Adsorption for dye house effluent by low cost adsorbent (Chitosan)", *Asian Textile Journal*, **10**(01), Jan (2001) 57-63

4. S. Asolekar and Yogita (Coordinators), Proceedings of NCUTE -Programme on "Environmental problems in chemical processing of textiles", Nodal Centre for upgradation of textile education (Ministry of textiles, GOI) IIT Delhi, Sept 21-22 (2000)

5. E.R.Trotmann, *Textile scouring and bleaching*, 1st ed (1993), B.I.Publications, N.Dehli

6. V.A.Shenai, *Technology of dyeing*, (1996) Sevak Publication, Mumbai

7. E.R.Trotman, *Dyeing and Chemical Technology of Textile Fibres*, 6th ed (1984) Charles Griffin and Co Ltd, London, England

8. Anon, "Colour in dye house effluents and decolorisation", *Colourage*, **LI (**12) (2004), 75-78

9. P.K.Goel, *Water Pollution, Causes, Effects and Control* (1997) New Age International (P) Ltd Publishers, New Delhi

10. S. M. Landage, "Removal of heavy metals from textile effluent", *Colourage*, **LVI** (6) (2009) 51-56

11. Arun Prasad and Kokati Venkata Bhaskara Rao**, "**Physico Chemical Analysis of Textile Effluent and Decolorization of Textile Azo Dye By *Bacillus Endophyticus Strain* Vitabr13", *The IIOAB Journal,* **2** (2) (2011)55-62

12. R.S. Lokhande, Pravin U. Singare, Deepali S. Pimple, "Pollution in Water of Kasardi River Flowing along Taloja Industrial Area of Mumbai, India", *World Environment,* **1**(1) (2011) 6-13

13. *Indian Standard,* DRINKING WATER — SPECIFICATION *(First Revision)* (Incorporating Amendment No. 1)UDC 628.1.033**,** IS 10500: 1991, Edn 2.1, (1993-01)

14. M.Kennedy, "Electrochemical wastewater treatment technology for textiles", *American Dyestuff Reporter*, **80**(9) (1991) 6–29

15. J.M. Randall, V. Garett, G. Bermann, and A.C. Waiss, "Removal and recycling of heavy metal ions from waste solutions", *Forest Product Journal*, **24**(9) (1974) 80-84

16. R. Suemitsu, R. Uenishi, I. Akashi and M. Nakano, "The use of dyestuff-treated rice hulls for removal of heavy metals from waste water" *Journal of Applied Polymer Science*, **31**(1)(1986)75-83

17. J.M. Randall, F.W. Reuter and A.C. Waiss, "Removal of cupric ion from solution by contact with peanut skins", *Journal of Applied Polymer Science*, **19**(6) (1975) 1563-1571

18. M.S. Masri, F.W. Reuter, M. Friedman, "Binding of metal cations by natural substances", *Journal of Applied Polymer Science*, **18**(3) (1974) 675-681
19. M. Friedman and A.C. Waiss, "Mercury uptake by selected agricultural products and by-products", *Environmental Science and Technology*, **6** (1972) 457-458
20. P.I. Norman and R. Seddon, "Pollution control in the textile industry - the chemical auxiliary manufacture's role", *Journal of Society of Dyers and Colourists*, **25**(4) (1991) 150-152
21. B. Martel, M. Devassine, G. Crini, M.Weltrowski, M. Bourdonnaeu and M. Morcellet, "Preparation and sorption properties of a β-cyclodextrin-linked chitosan derivative", *Journal of Polymer Science, Part A: Polymer Chemistry*, **39** (1) (2001) 169–176
22. G. Crini and P.M. Badot, "Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature", *Prog. Polym. Sci.*, **33** (2008) 399–447
23. J. A. Laszlo, "Removing acid dyes textile waste water using biomass for decolorization", *American Dyestuff Reporter*, **83**(08) (1994) 17-21
24. Brent Smith, T. Koonce and S. Hudson , "Decolorizing dye waste water using chitosan", *American Dyestuff Reporter*, **72**(10) October (1983) 18-36
25. N.M. Alves and J.F. Mano, "Chitosan derivatives obtained by chemical modifications for biomedical and environmental applications", *International Journal of Biological Macromolecules* , **43** (2008) 401–414
26. R. Jaykumar, M. Prabhaharan, R.L.Reis and J.F.Mano, "Graft copolymerization of chitosan- present status and applications", *Carbohydrate Polymers*, **62**, (2005) 142-158
27. Mohammad Hadi Mehdinejad, Bijan Bina, Mahnaz Nikaeen and Hossein Movahedian Attar, "Effectiveness of chitosan as natural coagulant aid in removal of turbidity and bacteria from turbid waters", *Journal of Food, Agriculture & Environment*, **7** (3&4) (2009) 845- 850
28. J.M. Randall, V. G. Randall, G. M. McDonald and R.N. Young, "Removal of trace quantities of nickel from solution" *Journal of Applied Polymer Science*, **23**(3) (1979)

727-732

29. Ruey-Shin Juang, Ru-Ling Tseng, Feng-Chin Wu and Shwu-Hwa Lee, "Adsorption behavior of reactive dyes from aqueous solutions on chitosan", *Journal of Chemical Technology and Biotechnology*,**70**(4)**,** (1997) 391-399
30. E. Guibal, M. Jansson-Charrier, I. Saucedo and P. Le Cloriec, "Enhancement of Metal Ion Sorption Performances of Chitosan: Effect of the Structure on the Diffusion Properties", *Langmuir* **11**(2)**, (**1995**)** 591-598
31. G. Karthikeyan, K. Anbalagan And N. Muthulakshmi Andal, "Adsorption dynamics and equilibrium studies of Zn (II) onto chitosan", *Journal of Chemical Sciences*, **116** (2), March (2004) 119–127
32. Saifuddin M. Nomanbhay and Kumaran Palanisamy, "Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal", *Electronic Journal of Biotechnology*, **8**(1) (2005) 43-53
33. Yang-Chuang Chang and Dong-Hwang Chen, **"**Recovery of Gold(III) Ions by a Chitosan coated Magnetic Nano-adsorbent**",** *Gold Bulletin***, 39**(3), (2006) 98-102
34. K.R.Holme and L.D.Hall, "Novel metal chelating chitosan derivative: attachment of iminodiacetate moieties via a hydrophilic spacer group" *Canadian Journal of Chemistry*, **69**(4) (1991) 585-589
35. R.A.A. Muzzarelli, F. Tanfani, M. Emanuelli, "Aspartate glucan, glycine glucan, and serine glucan for the removal of cobalt and copper from solutions and brines" *Biotechnology and Bioengineering*, **27**(8) (1985)1151–1157
36. I. Saucedo, E. Guibal, C. Roulph, P. Le Cloirec, "Sorption of uranyl ions by a modified chitosan: Kinetic and equilibrium studies", *Environmental Technology*, **13**(12) (1992) 1101–1116
37. K.Inoue, T.Yamaguchi, M.Iwaski, K.Ohto, and K.Yoshizuka, "Adsorption of Some Platinum Group Metals on Some Complexane Types of Chemically Modified Chitosan", *Separation, Science and Technology*, **30**(12) (1995) 2477-2487
38. E. Guibal, T. Vincent and R. Navarro Mendoza, "Synthesis and characterization of a thiourea derivative of chitosan for platinum recovery", *Journal of Applied Polymer Science*, **75**(1) (2000) 119–134
39. K. Kondo, S. Nakagawa, M. Matsumoto, T. Yamashita and I. Furukawa, "Selective

Adsorption Of Metal-Ions On Novel Chitosan-Supported Sulfonic-Acid Resin", *Journal Chemical Engineering*, **30**(4) (1997) 846–852

40. F.A. Abdel-Mohdy, M.S. Ibrahim, and S. El-Sawy, "Metal removal by chitosan and some chitosan composites", *Journal of The Textile Association*, **66** (5) Jan-Feb (2006) 219-226
41. N.F.Desai, "Profiles in Analysis of Chemicals", (1983), Gokul Publishers, Mumbai
42. Eskell Nordell, "*Water treatment for industrial and other uses*", (1951) Reinhold Publishing Corporation, N.York
43. S.R.Karmaker, "*Chemical Technology in the Pre-treatment Processes of Textiles*", Science and Technology-12, (1999) Elsevier Science B.V., Amsterdam
44. V.A.Shenai, *Technology of Bleaching and Mercerizing*, **III** (1996) Sevak Publication, Mumbai
45. Ping Li, Ya-Ni Dai, Jun-Ping Zhang, Ai-Qin Wang and Qin Wei, "Chitosan–Alginate Nanoparticles as a Novel Drug Delivery System for Nifedipine", *International journal of Biomedical science*, **4**(3) (2008;)221-228
46. Zofia Modrzejewska, Małgorzata Dorabialska, Roman Zarzycki and Anna Wojtasz-Pająk,"The mechanism of sorption of ag+ ions on chitosan microgranules: ir and nmr studies", *Progress on Chemistry and Application of Chitin and Its ...*, **XIV** (2009) 49-64
47. M.Reza Avadi, Gholamreza Mahdavinia Amini, Asal Mirmohammad Sadegi, Mohammad Irfan, Mohsen Amini, Morteza Rafiee Tehrani and Abbas Shafiee, "Synthesis and Characterization of N- Diethyl Methyl Chitosan", *Iranian Polymer Journal,* **13** (5) (2004) 431-436
48. A. Bayat, A.M.M. Sadeghi, M.R. Avadi, M. Amini, M. Rafiee-Tehrani, A. Shafiee and H.E. Junginger, "Synthesis of N, N-dimethyl N-ethyl Chitosan as a Carrier for Oral Delivery of Peptide Drugs", *Journal Bioactive and Compatible Polymers*, **21,** (2006) 433-444
49. P. L. Soni, *Inorganic chemistry*, 29th ed (2007) Sultan Chand Sons, N.Delhi ISBN 81-8054-585-7
50. C. L. Vel´asquez, J. S. Albornoz, and E.M. Barrios, "Viscometric stidies of chitosan

nitrate and chitosan chlorhydrate in acid free NaCl aq solution," *e-Polymers*, no.014 (2008)

51. J. K. Hwang and H. H. Shin, "Rheological properties of chitosan solutions," *Korea-Australia Rheology Journal*, **12** (3-4) (2000) 175–179
52. Mukesh K. Raikwar, Puneet Kumar, Manoj Singh and Anand Singh, "Toxic effect of heavy metals in livestock health", *Indian Veterinary Research Institute*, **1** (1) (2008)
53. A. K. Krishna and P. K. Govil, "Soil contamination due to heavy metals from an industrial area of Surat, Gujarat, Western India", *Environ Monit Assess*, **124** (2007) 263–275
54. Groundwater Quality Series:Gwqs/ 10/2007-2008, Status Of Groundwater Quality In India -Part-II, Central Pollution Control Board (Ministry Of Environment And Forests) April, (2008) 63
    Website: www.cpcb.nic.in
55. Perry D. Cohn, Michael Cox and Paul S. Berger, "Chapter 2: Health and Aesthetic Aspects of Water Quality" in *Water Quality and Treatment: A Handbook of Community Water Supplies*, Raymond D. Letterman (Edt), 5th edition, (1999), McGRAW-HILL, INC. New York, 83-89
56. Rong-Min Wang, Nai-Pu He, Peng-Fei Song, Yu-Feng He, Lan Ding and Zi-Qiang Lei, "Preparation of nano-chitosan Schiff-base copper complexes and their anticancer activity", *Polymers Advanced Technologies*, **20** (2009) 959–964
57. P. Rajaguru, K .Kalaiselvi, M.Palanivel and V. Subburam, "Biodegradation of azo dyes in a sequential anaerobic-aerobic system", *Applied Microbiology and Biotechnology*, **54** (2000) 268–273
58. D.P.Chattopadhyay, "Cationization of cotton for low salt and salt free dyeing ", *Indian Journal of Fibre & Textile Research*, **24,** March(2001)108-115
59. Grahame Birch and Keith Cockett, "Adsorption systems", Chapter 6 in *Water recycling in textile wet processing* (2003) J.Kenneth Skelly(ed) Society of Dyers and Colourists, West Yorkshire, England, 71-82
60. Warren S. Perkins, "Chemical oxidation and electrochemical systems", Chapter 7 in *Water recycling in textile wet processing* (2003), J.Kenneth Skelly(ed), Society of Dyers and Colourists, West Yorkshire, England, 83-151

61. Mark Carlough, Sam Hudson, Brent Smith, and Dawn Spadgeenske, "Diffusion coefficient of direct dyes in chitosan", *Journal of Applied Polymer Science*, **42** (1991) 3035-3038
62. G.McKay,H.S.Blair and J.Gardener, "The adsorption of dyes onto chitin in fixed bed columns and batch adsorbers", *Journal of Applied Polymer Science*, **29** (1984) 1499-1514
63. G.McKay, H.S.Blair and J.Gardener, "The adsorption of dyes in chitin.I. Equillibrium studies", *Journal of Applied Polymer Science*, **27** (1982) 3043-3057
64. Harry H.Sumner, "Thermodyanamics of dye sorption", *The theory of colouration of textiles*, 2nd edition (1989) Alan Johnson(ed), Society of Dyers and Colourists, West Yorkshire, England, 255-372
65. A. Domard, M. Rinaudo, and C. Terrassin, "New method for the quaternization of chitosan," *International Journal of Biological Macromolecules*, **8**(2) (1986)105–107
66. Kh.F.El.Tahlawy, "Utilization of citric acid-chitosan, sodium hypophosphite system for effecting concurrent dyeing and finishing", *Colourage*; **XLVI** (5) (1999) 21-26

CHAPTER 6
CONCLUSIONS

Chitosan is a versatile polycationic biopolymer derived from alkaline deacetylation of chitin. Chitosan exhibits several valuable inherent properties such as antibacterial, antifungal, antiviral, antacidity, chelation, non toxicity, biodegradability as well as film formation etc properties. Further, due to its possession of hydroxyl and amino functional groups, chitosan can be fabricated to tailor products with desired functional properties. Keeping in mind these valuable inherent properties and huge application potential, the aim of present study was focused on the applications of chitosan and its various derivatives in textile processing. The work was divided into four major areas:

(i) Synthesis of chitosan of different molecular weights and determination of effect of their applications on cotton fabric,

(ii) Synthesis of nano chitosan colloids and determination of effect of their applications on various properties of cotton fabric,

(iii) Synthesis of *N*-substituted chitosan derivatives and determination of effect of their applications on important properties of cotton fabric, and

(iv) Use of chitosan derivatives in the removal of metal ions from feed and drain water of textile processing.

Chapter 2:

Chapter 2 primarily included the studies related to applications of chitosan of varying molecular weights in wet processing of cotton fabric. From the findings of these experiments, following conclusions were drawn.

1. The molecular weights of parent chitosan samples, namely CHT and CHT-MC, were determined viscometrically. These supplied chitosan samples were characterized by FTIR spectroscopy and the structures of both the samples were found identical. Degree of deacetylation (DAC) of chitosan samples was determined by ^{1}NMR spectroscopy and elemental analysis and the values were in close agreement with the data provided by the manufacturer i.e. 90%.

2. Low molecular weight chitosans were synthesized by nitrous acid depolymerization method. The FTIR spectra of chitosan and depolymerized chitosan were almost identical indicating the process of depolymerization caused no chemical change in the structure of the polymer except reduction in molecular weight.
3. The viscosity of chitosan solution was found to be greatly influenced by its molecular weight. The initial molecular weight and the concentration of chitosan were found to influence the stability of its solution. The drop in viscosity in first 24 h was very fast and the critical concentration (C*) point shifted towards right when the storage time was prolonged. The stability of low molecular weight chitosan was not significantly affected within the chosen concentration range. The viscosity of chitosan solution was dropped due to the incorporation of electrolyte (sodium acetate); the effect was more prominent for high molecular weight chitosan solution. Therefore low molecular weight chitosans in presence of suitable electrolyte can be preferably used in textile applications.
4. The SEM of high molecular weight chitosan treated fibres was appeared to be glossy indicating the surface deposition of chitosan, while low molecular weight chitosan treated fibre surface was matty indicating non filmed surface.
5. The stiffness of the fabric was increased due to chitosan treatment which increased with increase in molecular weight and concentration.
6. The absorbency of the fabric was found to be reduced after chitosan treatment, which was deprecated with increase in molecular weight and concentration of chitosan. The drop in absorbency for high molecular weight chitosan treatment may be due to the formation of rigid film of chitosan over the fibre surface.
7. Substantial enhancement in dye uptake of cotton fabric was noticed due to chitosan pretreatment. The dye uptake was increased with increase in concentration and molecular weight of treated chitosan. The extent of improvement was more for the dyes having high molecular weight and containing more number of anionic (sulphonate) groups (e.g. C. I. Direct Blue 71). Almost a salt free dyeing was possible by chitosan pretreatments. But the fastness properties of chitosan pretreated and dyed samples were not satisfactory.

8. A stoichiometric amount of acid dye was taken up by the chitosan treated cotton fabric. Acid dye adsorption test can be employed as a tool for the characterization of chitosan and also the amino groups on cotton fibre.
9. Chitosan treatment did not, however, prove quite suitable for easy care finishing.
10. Chitosan treatment showed improved resistance to rotting in soil burial test. The resistance to microbial attack was due to concerted action of chitosan as polycationic nature, to form a rigid protective coating and as a chelating agent to scavenge the essential metal ions from cytoplasm of microorganism.

Chapter 3:

The very large molecular size and consequently high viscosity of chitosan restricts its penetration into the fibre and fabric structure and leads to only surface deposition. As a result adverse effects on several properties such as appearance, feel and poor fastness properties of dyed samples were observed. Today's need, however, is to improve above properties without altering the inherent natural qualities of cotton. In order to enhance the greater penetration without hampering the useful properties of chitosan, the particle size was reduced to near nano scale by ionotropic gelation technique using TPP as crosslinker. Following conclusions were drawn from the findings of experiments of chapter 3.

11. The particle size and size distribution of the chitosan were analyzed using particle size analyzer.
12. The concentration of chitosan in the formulation bath was found to influence the size of particle. Particle size was reduced with reduction in concentration. Direct preparation method produced particles with comparatively lower size than that found in dilution method.
13. Reduction in molecular weight and in turn drop in intrinsic viscosity decreased the particle size and showed a curvilinear dependence. This relation may be useful in preparation of nano chitosan dispersion of desired particle size.
14. TPP concentration was found to play an important role in controlling the particle size. With increase in concentration of TPP, the particle size was first reduced, reached to minimum and again increased. Excessive TPP led to precipitation.

15. Reduction in particle size reduced the viscosity of chitosan solution significantly, but the storage stability was affected adversely. Use of freshly prepared nano-chitosan dispersions prior to applications may be the remedy.
16. The appearance and handle of nano chitosan treated cotton fabric was much better than the parent chitosan treated one.
17. Nano chitosan treatment showed improvement in fibre strength that increased with the reduction in particle size.
18. Nano chitosan treatment reduced the water absorbency to some extent.
19. The dyeability of both chitosan and nano chitosan treated cotton fabric towards direct dyes was improved reasonably. Acidification of dye bath further improved the dye adsorption and wash fastness of dyed fabric.
20. Nano chitosan together with nano silver treatment showed enhanced resistance to microbial attack.

Chapter 4:

In this chapter synthesis of a series of *N*-substituted chitosan is reported. There were three categories of product viz trimethyl chitosan chloride, *N*-alkyl substituted quaternized chitosan and *N*-aryl substituted quaternized chitosan. From the syntheses and application point of view, following conclusions were drawn.

21. The quaternization of chitosan was characterized by FTIR analysis. The degree of quaternization (DQ) of trimethyl chitosan chloride was determined conductometrically which was in close proximity to that determined by ^{1}HNMR and CHN analysis.
22. DQ of trimethyl chitosan chloride was increased progressively with the increase in concentration of methyl iodide. An optimum amount of alkali (NaOH), co-solvent (NMP) and electrolyte (NaI) was found to be essential to enhance the forward reaction in synthesizing trimethyl chitosan chloride.
23. Different *N*-alkyl chitosan derivatives namely *N*-ethyl, *N*-butyl and *N*-dodecyl; and *N*-aryl chitosan derivatives namely *N*-benzyl and *N*-(1-Naphthyl) methylene chitosan derivative were synthesized by reductive amination of Schiff's base formed by reaction between chitosan and corresponding aldehydes. Characterization was

performed through FTIR for qualitative and conductometry, ^{1}HNMR and CHN analysis for quantitative analysis of *N*-alkyl/aryl *N,N* dimethyl chitosan derivatives.

24. The degree of substitution was dropped with the increase in the chain length of alkyl substituent. Aryl substituents produced lower degree of substitution compared to corresponding alkyl counterpart. The DQ of *N*-alkyl and *N*-aryl chitosan derivatives was decreased with the increase in the molecular size of substituents.
25. The intrinsic viscosity was dropped due to quaternization. Higher the size of the substitution higher was the viscosity. Viscosity of all *N*-substituted quaternized chitosan solutions ware lower in presence of electrolyte. Quaternized chitosan solutions have shown paradoxical behaviour in absence of electrolytes i.e. viscosity increased at high dilutions.
26. *N*-modified chitosan derivatives were applied to cotton fabric by pad-dry cure technique. The appearance of cotton fabric was found to be comparatively improved by it's treatment with quaternized chitosan as against normal chitosan treatment. The feel of the treated fabric was improved with the increase in the chain length of *N*-alkyl substituents. *N*-aryl chitosan derivatives showed moderate improvement in handle.
27. The chlorine retention problem occurred due to chitosan treatment on cotton fabrics was reduced substantially by quaternization of chitosan.
28. The absorbency of trimethyl chitosan chloride treated cotton fabric was improved progressively with the increase in the degree of quaternization. The absorbency of *N*-alkyl/aryl chitosan derivatives treated cotton fabric was dropped.
29. Quaternized chitosan treated fabric showed enhanced dyeability towards direct dye with improved washing fastness properties. The dye uptake was increased with increase in the DQ. It also showed satisfactory dye uptake in absence of electrolyte in the dye bath.
30. Trimethyl chitosan treated cotton fabric showed stoichiometric amount of acid dye adsorption in neutral dye bath.
31. The wrinkle recovery property of cotton fabric was improved to some extent due to *N*-substituted quaternized chitosan derivatives treatment.

32. The chitosan treated samples were soiled more compared with the control one. The quaternization of chitosan was found to improve the soil release properties. The degree of soiling was found to get reduced with the increase in DQ.
33. The quaternization of chitosan was found to improve the resistance towards microbial attack and was improved with increase in the degree of quaternization.

Chapter 5:

Textile wet processing operations produce high volumes of waste water of varying composition that may be harmful to health and environment. It is, therefore, extremely essential that the environmental problems associated with industrial developments are properly addressed for sustainability. As a part of this work, it was found that the presence of excessive amount of calcium in feed water reduced the dye uptake while copper ions reduced the bleaching efficiency of hydrogen peroxide and produced off shades in direct and reactive dyeing. The present investigation (chapter 5) was, therefore, aimed at the understanding the chelation behaviour of chitosan and its derivatives for calcium and copper ions and as a sorbent for removal of traces of dyes from waste water. Chitosan of different molecular weights and quaternized derivatives of varying degree of quaternization were employed in the present experiment. The effect of particle size of chitosan on scavenging efficiency was also examined. From the findings, following conclusions were drawn.

34. The binding of calcium and copper ions to chitosan was confirmed by FTIR. The attachments were mostly effected through coordinate linkages with *O* and *N* of chitosan. The results of iodometric titration method employed for the determination of residual copper ions in water were found to be comparable to that found using atomic absorption spectrometry (AAS). Copper ions adsorbed on chitosan were determined gravimetrically.
35. The chelation behaviour of chitosan derivatives towards calcium and copper ions was found to be almost similar except the extent of sorption capacity which was higher for copper ions.
36. The rate of chelation for metallic ions like calcium and copper was found to be decreased with the increase in the molecular weight of chitosan. The sorption of these

ions was increased with increase in concentration of chitosan. The extent of chelation was found to be high for low molecular weight chitosan when treated for shorter time and decreased with increase in the molecular weight. However very high concentration of chitosan, high molecular weight in particular, is not desirable due to viscosity problems.

37. Highly acidic pH was not found to be suitable for chelation of metal ions. A milder acidic condition (pH 5.5) showed better results.
38. Reduction in particle size of chitosan enhanced both the rate and amount of scavenging of metal ions.
39. The chelation efficiency of trimethyl chitosan was reduced with increase in the degree of quaternization.
40. Chitosan and trimethyl chitosan derivatives were found to be useful adsorbents for colour waste water treatment. Trimethyl chitosan derivative was effective at neutral pH where as normal chitosan required acidic pH. Subsequent mild alkalization could precipitate the chitosan-dye complex and reduce the turbidity.

FUTURE PROSPECTS…

Use of biodegradable and not toxic products from 'natural' sources is growing rapidly and becoming more and more appealing for the replacement of synthetic compounds. Chitosan is a unique polymer that has demonstrated utility in number of applications in textiles. Chitosan, nevertheless, is a versatile product but it requires suitable modifications so that it can be judiciously employed for desired end uses. Therefore, a single product may not necessarily be suitable for all unit operations of textile processing. Therefore suitable structural modifications of chitosans and use of nano technology or combination of both may open a new avenue for its intelligent textile application. In water processing, chitosan may be more suitable for removal of metal ions which may be present in traces i.e. ppm or ppb rather than for industrial or dye house discharge that contains large amount of impurities or else it may used as a sorbent for the isolation of precious metals such as silver, gold or radioactive elements. Introduction of suitable groups or ligands in the backbone of chitosan can enhance its scavenging power and also preference for chelation of specific metal ions.

REPRINTS OF PAPER PUBLICATIONS

Textile Research Journal: Acceptance letter
Manuscript ID TRJ-13-0412.R2

---------- Forwarded message ----------
From: <dzhang@charter.net>
Date: Thu, Jan 9, 2014 at 11:09 PM
Subject: Textile Research Journal - Decision on Manuscript ID TRJ-13-0412.R2
To: dpchat6@gmail.com, rishichat7@gmail.com

09-Jan-2014

Dear Dr. Chattopadhyay:

It is a pleasure to accept your manuscript entitled "Application of chitosan and its derivatives in removal of Cu(II) ions from water used in textile wet processing" in its current form for publication in the Textile Research Journal.

Thank you for your fine contribution. You should also receive another e-mail to show you how to finish the author agreement form on-line. For the new online author agreement, what you need to do it:

1. read the agreement
2. at the end of the agreement, check the "I accept" box if you agree all the terms and conditions.

So your paper can be further processed for publication. Please let me know if you have any questions for it.

If you would like your article to be freely available online immediately upon publication (as some funding bodies now require), you can opt for it to be published under the SAGE Choice Scheme on payment of a publication fee. Please simply follow the link to the Contributor Agreement form in the next email and you will be able to access instructions and further information about this option within the online form.

To help support the cost of wide dissemination of research, the author is required to pay a publication charge.
The publication charge is currently US$775 per article. Payment of this charge entitles an author to access to 50 complimentary e-prints. Additional reprints can be purchased and timely payment of publication charges is expected. No charge will be imposed for publishing constructive criticism of an article that has previously appeared in the Textile Research Journal or any rebuttal comments. There is no extra charge for pictures, graphs, and text to appear in color online however additional charges will be imposed for color pictures, graphs, and text in print when requested by the author.

On behalf of the Textile Research Journal, we look forward to your continued contributions to the Journal.

Sincerely,
Dr. Dong Zhang
Editor in Chief, Textile Research Journal
dzhang@charter.net

(Paper accepted by Textile Research Journal, Manuscript ID TRJ-13-0412.R2, Acceptance Date 09-Jan-2014)

Application of chitosan and its derivatives in Cu(II) ions removal from water used in textile wet processing

D. P. Chattopadhyay*
Department of Textile Chemistry, Faculty of Technology & Engineering,
The M.S.University of Baroda, Vadodara-390001, INDIA

M. S. Inamdar
Faculty of Textile Processing, Sarvajanik College of Engineering &Technology, Surat-395001, INDIA

*Corresponding author: Cell: +91 9898251570; fax: +91-265-2423898; email:dpchat6@gmail.com

Abstract
The applicability of chitosan, trimethyl chitosan chloride and nano chitosan for removal of Cu(II)ions from water used in textile wet processing was studied. The liquor before and after treatment was analysed iodometrically for knowing the presence of Cu(II) ions and FTIR spectroscopy was employed for the characterization of Chitosan-Cu(II) complex. Study included the effect of molecular weight of chitosan, particle size of chitosan and the degree of quaternization of trimethyl chitosan chloride, pH of medium etc on the sorption of Cu (II) ions. The influence of molecular weight of chitosan was found to be an important criteria so far on rate of sorption of Cu(II) ions. Reduction in particle size of chitosan enhanced both the rate and amount of scavenging of metal ions.

Keywords: Chitosan, chelation behaviour, copper ions, nano-chitosan, trimethyl chitosan chloride

Introduction

Plentiful supply of good quality water is indispensable for textile wet processing industry. Water is not only a vehicle to carry or fix the chemicals and dyes, but it is the medium for processing [1]. The water employed for various wet processing operations is now-a-days largely obtained from underground source which is accompanied with various heavy metal ions. The recycled water from effluent discharge also contributes to these impurities due to the inefficiency of conventional effluent treatment plants to remove such traces of metal ions. The presence of these ions, even in ppm level, can have detrimental effects on processes like enzymatic desizing, hydrogen peroxide stability and its bleaching action, shade of dyes etc [2, 3].

Among various metal ions, Cu (II) ion has gained attention due to its both beneficial and as well as adverse effects. Use of copper compounds such as copper sulphate in certain dyeings, direct dyeing in particular, has found to improve the fastness to washing and light. However, presence of copper in water can seriously affect the performance of various unit operations of textile processing such as desizing, scouring, bleaching, dyeing etc. Hence it is advised to avoid copper/brass fittings especially in bleaching plants. Copper is found to be adsorbed by enzyme molecules to form complexes and inactivate the enzymatic action. Copper exhibits a catalytic action on hydrogen peroxide decomposition. Presence of copper is reported to cause instability in peroxide bleaching baths and damage the cotton during bleaching. Copper is readily absorbed on wool and therefore causes damage during peroxide bleaching. Presence of copper ions causes deleterious effect on the shades of various dyes used for cellulose, nylon and protein fibres; nevertheless it enhances the wash and light fastness properties [2, 4].The deleterious effect of Cu(II) ions observed on hydrogen peroxide bleaching of scoured cotton fabric and various direct and reactive dyeing of cotton is presented in Table1 and Figure1. Copper content in textile and allied industries effluent was found to be approximately 77 mg/L [5] as against the WHO norms 0.05 mg/L[5]. Traces of copper (5-45 µg/L) in underground water and about 110 mg/kg of soil in and around Surat (India) have been detected [6].

Table 1 Effect Cu(II) ions on hydrogen peroxide bleaching of cotton fabric

$CuSO_4$ content in bleach bath, mg/L	Whiteness index	Yellowness index	Brightness index
Control	88.40	1.33	78.08
100	85.98	4.29	73.02
200	85.06	4.69	71.17
500	84.14	5.58	69.32

*Scoured sample***:** *W.I. = 78.07, Y.I. = 17.02 and B.I. =56.91*

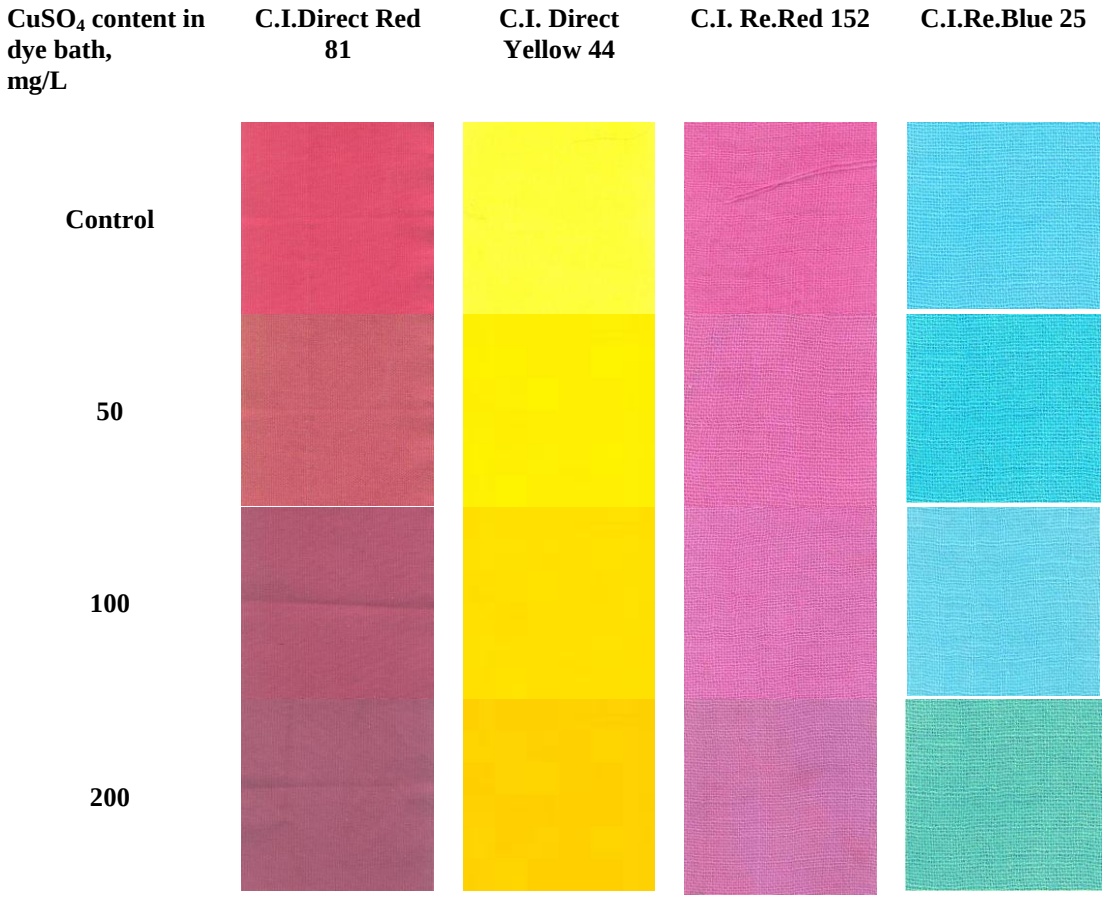


Figure 1 Effect of Cu (II) ions in dye bath on the shades of direct and reactive dyeing on cotton fabric

The adverse effect of such metal ions can be controlled either by using chelating agents like ethylene diamine tetra acetic acid (EDTA), diethylene triamine penta acetic acid (DTPA), nitrilo triacetic acid (NTA) etc [7] or metal ions can be chemically precipitated or coagulated as salts or reduced to metallic form. They can be separated out from the liquid phase by filtration, settling, centrifuging or electro deposition [1,8,9]. Various natural products such as wood bark and clay [10], rice hull, cotton fibres, bamboo pulp, peanut skin etc and chitosan have been found to remove metal cations from the streams [11-14]. The detrimental effects on environment still persist when water is treated through first route due to the existence of metal ions in discharged water, while metal ions are removed from discharged water by second route is safer.

Chitosan is a natural based product derived from alkaline deacetylation of a biopolymer, chitin. It is second most abundant biopolymer after cellulose. The amount of presence of primary amino groups present on chitosan molecule is characterized by degree of deacetylation (DAC) [15]. The application potential of chitosan and its derivatives for the recovery of valuable metals or the treatment of contaminated effluents is well documented [16, 17]. Our earlier report [18] has shown the scavenging

property of chitosan for calcium ions. Karthikeyan et al. [19] studied the dynamics and equilibrium sorption of Zn (II) on to chitosan. They observed maximum of six minutes were required for complete sorption of Zn ions by chitosan obeying the Freundlich and Langmuir isotherms. Nomanbhay and Palanisamy [20] used chitosan coated oil palm shell charcoal successfully for the adsorption of chromium ions from water. Bioconversion of highly toxic Cr(VI) into Cr(III) was also observed, which is essential in human nutrition especially in glucose metabolism. Chang and Chen [21] isolated Au (III) ions from water on chitosan coated Fe_3O_4 nanoparticles. They found that the gold ions could be fast and efficiently adsorbed. E.Guibal et al.[22] synthesized thiourea derivative of chitosan for platinum and mercury recovery owing to the chelating affinity of sulphur ligands. Abdel Mohdy et al. [23] introduced diethyl amino ethyl methacrylate (DEAEMA) groups onto chitosan backbone through radiation grafting and studied the chelation property of grafted derivative on copper, zinc and cobalt ions. They reported that the extent metal ions uptake by chitosan-DEAEMA derivative was preferentially higher for copper ions followed by zinc and cobalt ions. The present investigation was aimed at understanding the chelation property of chitosan and its derivatives towards Cu(II) ions. Chitosan of different molecular weight, nano chitosan of varying particle size and trimethyl chitosan derivative of different degree of quaternization were taken for the study. The test sample before and after treatment was analysed iodometrically for knowing the presence of Cu(II) ions and FTIR spectroscopy was employed for the characterization of Chitosan-Cu(II) complex.

Materials and Methods

Materials: 100% cotton fabric (warp and weft 40s, ends/inch142, picks/inch 72 and g/m^2 125), at ready for dyeing stage, was procured from Mafatlal Industries Ltd, Nadiad, Gujarat State,India. Chitosan of different molecular weights were obtained from Marine Chemicals, Kerala State, India (CHT-MC) and Mahtani Chitosan Pvt. Ltd., Gujarat State, India (CHT). A low molecular weight chitosan (CHT-D) was synthesized from CHT by depolymerization with nitrous acid as described earlier [25]. The specifications of different grades of chitosan are given in Table 2. Various direct and reactive dyes namely C.I.Direct Red 81, C.I. Direct Yellow 44, C.I. Reactive Red 152 and C.I. Reactive Blue 25 were kindly supplied by Colourtex Industries Ltd, Gujarat State, India. Anionic detergent (Ezee, Godrej, India) employed was of commercial grade.

Other reagents like Acetic acid, Acetone, Methyl alcohol, Methyl Iodide, EDTA, Sodium thiosulphate, Potassium iodide, Sodium iodide, Sodium hydroxide, Soda Ash, Sodium sulphate, Copper sulphate, N-methyl-2-pyrrolidone (NMP) etc used were of analytical grade.

Synthesis of trimethyl chitosan chloride

Trimethyl chitosan chloride (TMCHT) was synthesized as follows: purified chitosan (CHT) (1g) was treated with required amount methyl iodide (5 g and 15g for two different levels of degree of quaternization) in presence of sodium iodide 2.4g and sodium hydroxide (2g) dispersed in N-methyl-2-pyrrolidone (NMP)(40 mL) in a stainless steel reaction vessel at 50^0C for 24h. Trimethyl chitosan iodide was recovered from using acetone then subjected to ion exchange by treatment with sodium chloride (10%, 50 mL) for 1h. TMCHT was then recovered from acetone with repeated washings and oven dried at 55^0C.

Synthesis of Nano chitosan dispersions

The method for synthesis of nano chitosan dispersions was followed same as discussed elsewhere [18]. The prepared nano-chitosan (CHTN) from the starting material CHT was stored in refrigerator. The particle size and size distribution of the chitosan were analyzed on the particle size analyzer (Zetasizer Nano ZS90, Malvern Instruments Ltd, UK).

Hydrogen peroxide bleaching of cotton fabric

Scoured cotton fabric was treated with solution containing hydrogen peroxide (30%, 10 g/L), soda ash (10 g/L) sodium silicate (10 g/L), and detergent (1 g/L) at about 85 ^{0}C for 60 minutes. The material- to- liquor ratio was maintained at 1:30. After bleaching was over, the fabric was washed at 80 ^{0}C for 20 minutes and then rinsed.

Dyeing with Direct Dyes

The cotton fabric was dyed with direct dye (1% o.w.m.) in presence of Glauber's salt (20% o.w.m.) and soda ash (5% o.w.m.) at temperature 90 ^{0}C for 60 minutes. The material- to- liquor ratio was maintained at 1:40. The dyed sample was then rinsed with cold water 3 times, air dried and hot pressed. The dyed

samples were evaluated for colour strength in terms of K/S values on computer colour matching system (Spectroscan 5100A, Premier Colorscan, India).

FTIR Analysis

FTIR of CHT and TMCHT derivatives were taken on a Thermo Nicolet iS10 Smart ITR spectrophotometer (Thermo Fisher Scientific, USA) in the wavenumber between 4000–500 cm^{-1}.

Treatment of Cu(II) ions containing water with chitosan derivatives

Required quantity of chitosan or chitosan derivative (e.g.1g/L) was treated with copper sulphate solution corresponding to Cu(II) ions concentration of 394.32 mg/L in presence of acetic acid (0.7 mL/L for pH 5.5 and 1.5 mL/L for pH 3.5) with occasional stirring. After the prescribed reaction time is over, chitosan was precipitated out by the addition of few drops of sodium hydroxide (10%) solution. The solution was then filtered, the filtrate was analysed for Cu(II) ions content iodometrically and the residue was analysed for FTIR spectroscopy.

Iodometric method for determination of Cu(II) ions

100 mL aliquot (sample solution) was taken in a conical flask and mixed with 10 mL of 10% liquor ammonia to obtain a dark blue colour. The solution was then neutralized with acetic acid; a slight excess acid was added, followed by 2 g of potassium iodide. The flask was placed in dark for about 15 minutes for complete liberation of free iodine and then titrated against 0.1N sodium thiosulphate using starch as indicator. Ammonium thiocyanate (2 g in 10 mL water) was then added and titration continued. The amount of Cu(II) present in the given solution was calculated following equation [25].

$$\text{Cu(II) ions content, mg/L} = \frac{A \times 6.36 \times 1000}{V}$$

Where, 'A' is the amount (mL) of 0.1N $Na_2S_2O_3$ taken in burrette and 'V' is thevolume (mL) of aliquot taken for titration (100 mL)

$$\text{Chelation efficiency in terms of sorption of Cu(II) ions by chitosan (mg/g)} = \frac{I_0 - I_F}{M}$$

$$\text{Chelation efficiency in terms of copper ions removal from water (mg/L)} = I_0 - I_F$$

Where, I_0 is the initial concentration (mg/L) of Cu(II) ions and I_F is the concentration(mg/L) of Cu(II) ions in treated water. M is the mass (g) of chitosan.

Results and Discussion

Characterization and mechanism of chelation of copper (II) ions on chitosan

The important ligands on chitosan macromolecule that form complex with metal ions are oxygen pertaining to primary and secondary hydroxyl groups and nitrogen belonging to amino and acetamido groups. The structural changes in chitosan occurred due to chelation with Cu(II) ions can be conveniently studied using FTIR spectra analysis. The FTIR spectra of CHT and CHT-Cu complex are presented in Figure 2 and Figure 3.

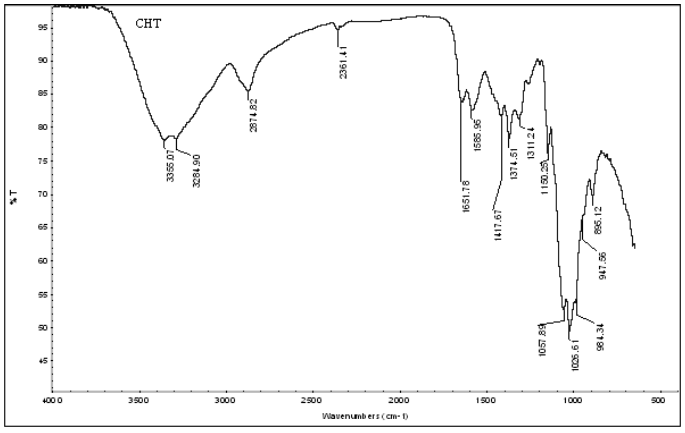


Figure 2 FTIR spectrum of CHT

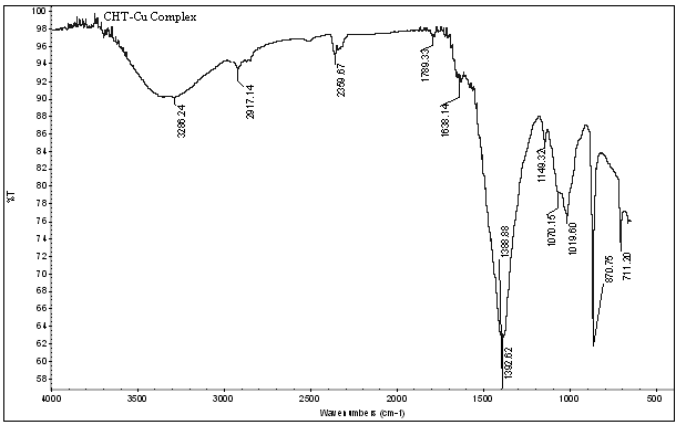


Figure 3 FTIR spectrum of CHT-Cu complex residue

The broad bands at wave numbers 3355, 3284cm^{-1} of the FTIR spectrum of chitosan (Figure 2) may be attributed to O-H, NH and NH_2 stretching. The absorption band at 1651 cm^{-1} was due to C=O (carbonyl) stretching of secondary (amide I) amide bond, a characteristic of N-acetyl group and the medium peak at 1585 cm^{-1} appeared due to bending vibrations of N-H of amide II bond (N-acetyl residue) and the primary amine. Another medium absorption peak at 1374 cm^{-1} was attributed to the N-H linkage of amide III. A strong absorption peak at 1025 cm^{-1} was due to primary hydroxyl group, characteristic peak of -CH_2OH in primary alcohols, arised from C-H stretching [26, 27]. The structural changes in chitosan arised due to complex formation with copper ions were observed in the spectrum as shown in Figure 3. The broadening of the peak at 3355 cm^{-1} and progressive reduction of peak at wave number at 1025cm^{-1} indicated the involvements of amino and hydroxyl groups in the scavenging of the Cu(II) ions. Formation of a new peak at 1392 cm^{-1} and modifications in peaks due to various amide groups characterized interaction of these groups with Cu(II) ions [28]. The complex formation of chitosan with copper ions may be explained with the help of its electronic configuration of copper ions. Copper, though not strictly termed as transition metals as their *d* orbitals are complete, still they form a number of complexes when their ions have incomplete *d* orbitals e.g. in the case of Cu(II) ions having the coordination numbers usually 2,4,and 6 facilitate coordinate bond formation [29]. The possible ways of Cu(II) ions bound to chitosan is illustrated in Figure 4.

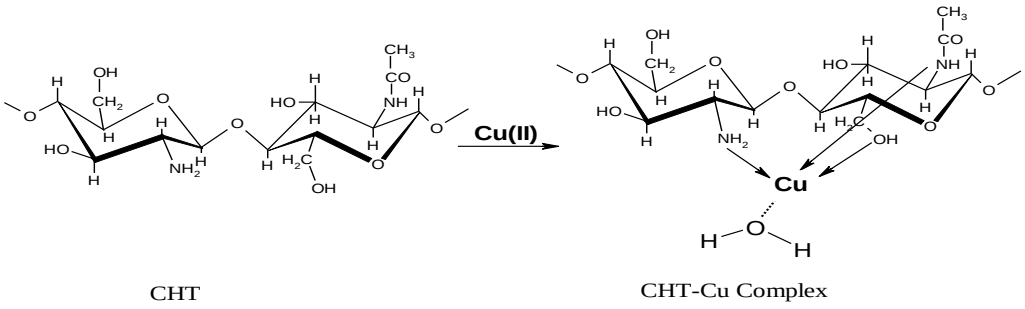


Figure 4 Chelation of Cu (II) ions by chitosan

In order to understand the chelation property, chitosans in various forms and grades were employed as listed in Table 2 and the performance were compared with tetra sodium salt of ethylene diamine tetra acetic acid (Na_4EDTA).

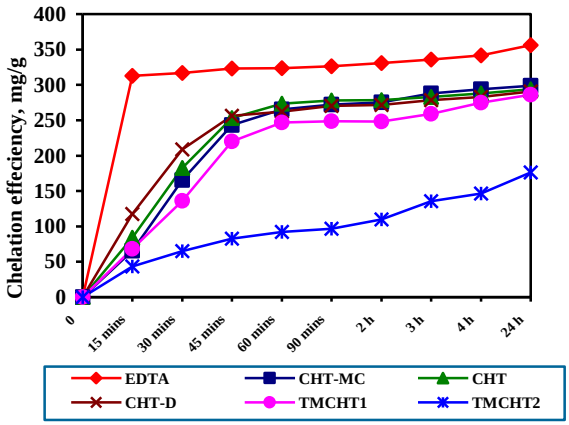
Table 2 Chitosan derivatives employed for chelation study

Sample code	Chemical Name	Properties			
		DAC, %	Molecular weight	Particle size, nm	DQ, %
CHT-MC	Chitosan	89.03	654,127	-	-
CHT	Chitosan	90	135,839	4014	-
CHT-D	Chitosan	90	38,733	-	-
CHTN1	Nano-chitosan	-	-	408.73	-
CHTN2	Nano-chitosan	-	-	534.2	-
TMCHT1	Trimethyl chitosan chloride	-	-	-	13.41
TMCHT2	Trimethyl chitosan chloride	-	-	-	50.92

DAC: Degree of deacetylation, DQ: Degree of quaternization

Effect of structural modification of chitosan on chelation of Cu (II) ions

The extent of copper ions binding of chitosan is believed to be dependant on the availability of number of electron donating ligands such as O and N. The state of these ligands on chitosan macromolecules is anticipated to be altered due to chemical modifications such as quaternization. The Cu(II) ions sorption by various chitosan derivatives at pH 5.5 is shown graphically in Figure 5.



Concentration of chelating agent 1g/L, Initial concentration of Cu(II) ions 394.32 mg/L, pH 5.5

Figure 5 Chelation behaviour of chitosan derivatives for Cu(II) ions

Figure 5 illustrates that EDTA attained the equilibrium rapidly for the copper ions binding and the chelation capacity was maximum. The prolong treatment showed little improvement in chelation efficiency after initial 15 minutes treatment. The chelation behaviour of chitosan was comparatively slower. The molecular weight of chitosan was found to have a little effect on its chelation behaviour. At the onset and during the first hour of treatment, the rate of chelation was slightly higher for low molecular weight chitosan. When the treatment was continued for longer time the copper ion sorption was levelled off for different molecular weight chitosans. With increase in molecular weight of chitosan (CHT-MC), the rate of sorption of copper ions was slowed down but the absolute adsorption after prolong treatment (>3h) was higher. Thus, the influence of molecular weight of chitosan, in first hour of treatment, seemed to be more pronounced on the rate of sorption rather than on absolute sorption of copper ions. Modification of chitosan by quaternization process was found to reduce its metal binding capacity. The chelation capability of trimethyl chitosan (TMCHT) was decreased with increase in degree of quaternization.

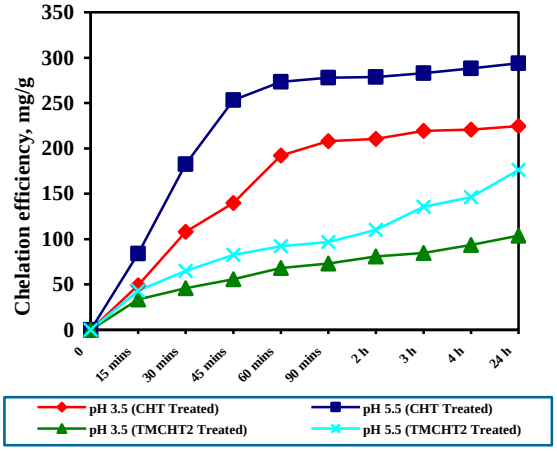
A substantially higher chelation power of EDTA may be attributed to the combined effect of ionic linkages of Cu(II) cations with anionic carboxylate groups and the coordinate bonds with amino groups. The electrostatic attraction between EDTA and metal cations may be the driving force for the attachments. Chitosan, on the other hand, is a polymeric material having rigid conformation. When dissolved in water in presence of acid, most of the amino groups are protonated and therefore are incapable of bonding with

copper cations. The only possible route of interaction is through unprotonated amino groups, hydroxyl groups and/or N-acetyl groups. Further, these polycationic macromolecules in solutions are mostly swollen entangled bunches exposing very small surface area and hence provide less ligands for interaction with metal ions. The chitosan molecules, therefore, are slower in chelation compared with EDTA. The latter inactivates metal ions but does not remove them. On the other hand, Chitosan, a biodegradable chelating agent, removes metal ions even when present in traces. The process can be made faster by using nano chitosans, chemical modifications of parent chitosan etc. It is a better choice for medical usage. Being polycationic polymeric material, chitosan can easily undergo sedimentation due to nucleation and can be removed simply by decantation or by sand filtration. On account to this unique property, chitosan can be used to minimize the turbidity in water treatment. Since the treatment is done prior to final filtration, no additional filtration is required.

The availability of accessible interactive ligands for chelation is determined by the physical state of macromolecules in solvent which in turn is determined by its molecular size and hence the molecular weight. Low molecular weight chitosans (CHT-D) in solution are comparatively more extended and mobile due to less intra and intermolecular forces and thus provide more surface area for chelation reactions and therefore shows enhanced rate of sorption. Conversely, high molecular weight chitosan (CHT-MC) molecules in solution are more entangled and compact with lesser accessibility of ligands which led to lower rate of sorption of Cu(II) ions. On prolong treatment, large sized chitosan molecules slowly under goes depolymerization due to hydrolysis, which results in fall in viscosity as was observed earlier[18] leading to opening of sites and continued chelation. The chelation property of trimethyl chitosan chloride (TMCHT), however, was reduced as some of the amino groups were engaged in forming bonds with methyl groups which consume the lone pair of electrons of nitrogen and also the presence of bulkier methyl groups restricts the diffusion of metal ions. For unmodified chitosans, recycling of the used product would be difficult as the attachment of metal ions to chitosan is accomplished by the coordinate linkages. But chemical modification of chitosan by introducing anionic groups like carboxyl, sulphonate etc can impart ion exchange property. The treatment of chitosan is effective in removing traces of metal ions and hence can be beneficial in isolation of precious metals

Effect of pH on chelation of Cu (II) ions

An important parameter that alters the state of ligands on chitosan and its derivatives is the pH of medium. Acidic pH is required for dissolution of chitosan in aqueous medium; however, it leads to protonation of amino groups. In order to understand the effect of pH on chelation behaviour of CHT and its quaternized derivative of maximum degree of quaternization i.e.TMCHT2, two different pH were selected namely pH 3.5 and pH 5.5. Higher pH (pH ~7) was avoided due to the formation of hydroxides of copper causing precipitation [30]. The sorption of Cu(II) ions by CHT and TMCHT2 as a function of pH is presented in Figure 6. CHT was found to be more efficient in complex formation with Cu(II) ions at pH 5.5. Similar results were observed in case of TMCHT2 though found to be less efficient compared with CHT. It is known that the attachment of Cu(II) ions with chitosan is possible through co-ordinate bonds by the donation of lone pair of electrons of amino, acetamido and hydroxyl groups. In highly acidic medium i.e. at pH 3.5 most of the amino groups are protonated and therefore they do not remain available for coordinate bond formation. In that case the scavenging of Cu(II) ions would be assigned to hydroxyl and N-acetyl groups. At slightly higher pH (pH 5.5), some of amino groups remain unprotonated or free. The free amino groups, due to the presence of lone pair of electrons, are capable of forming coordinate linkages with copper ions and hence an improvement in chelation was observed at pH 5.5. TMCHT exerts ionic repulsion to copper cations and in addition the bulkier side methyl groups act as a barrier and leads to the reduction in chelation efficacy of trimethyl chitosan.

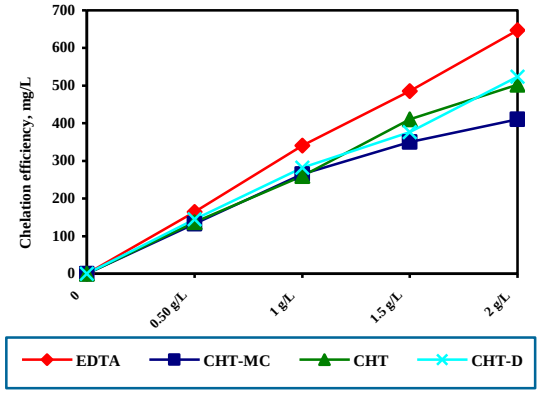


Concentration of chelating agent 1g/L, Initial concentration of Cu(II) ions 394.32 mg/L

Figure 6 Effect of pH of the medium on the chelation behaviour of chitosan derivatives at different time intervals

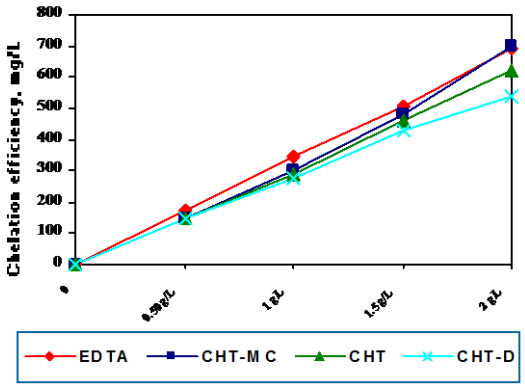
Effect of concentration of chitosan derivatives on chelation of Cu(II) ions

An important parameter that influences the sorption of metal ions is the concentration of chelating agent. The aqueous behaviour of chitosan was found to be governed by the storage time and the behaviour of chitosan in solution may affect the chelation capacity [20]. Thus, in order to understand the chelation behaviour, the effect of different concentration and molecular weights of chitosan on the removal of copper ions from water for two different durations of treatment, namely, short (1h) and long (24h) treatment time respectively was studied. The results are shown in Figure 7 and Figure 8.



Initial concentration of Cu(II) 754.93mg/L, pH 5.5

Figure7 Effect of concentration and molecular weight of chitosan on chelation efficiency for 1h treatment



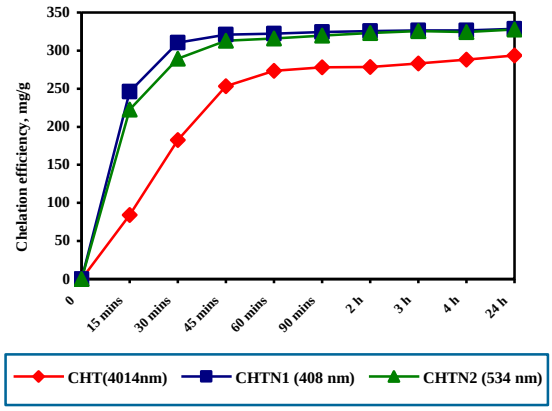
Initial concentration of Cu(II) 754.93mg/L, pH 5.5

Figure 8 Effect of concentration and molecular weight of chitosan on chelation efficiency for 24h treatment

It is observed from Figure7 and Figure 8 that the sorption curves for EDTA followed linearity with respect to concentration and almost same level of chelation efficacy observed for both the durations of treatment. The amount of Cu(II) ions removed from treated liquor was found to be increased with increase in concentration of chitosan derivatives. The sorption curve for low molecular weight chitosan (CHT-D), when treated for short time (1h), was found to be linear within chosen concentration range while high molecular weight chitosans showed some deviations at higher concentrations (Figure 7).The chelation efficiency of different forms of chitosan was found to follow the following trend CHT-D>CHT>CHT-MC. On prolong treatment i.e. when the treatment was extended to 24 h (Figure 8), the chelation behaviour of chitosan was altered particularly for high molecular weight chitosans. The chelation behaviour of low molecular weight chitosan (CHT-D) was not much influenced. The chelation efficiency of chitosans was, however, reversed as against short duration of treatment i.e. CHT-MC>CHT>CHT-D. The linearity observed for low molecular weight chitosan (CHT-D) can be ascribed to the presence of their molecules in solutions in comparatively free and more extended form due to less intra and intermolecular forces. These molecules provide, in chosen concentration range, uniform number of sites proportional to the concentration of chitosan. During short treatment time, high molecular weight chitosan (e.g. CHT-MC) molecules in solution still remain entangled due to overlapping of macromolecules as revealed by the viscosity measurement reported elsewhere [18]. Therefore they provide fewer sites for the interaction with Cu(II) ions resulting in to decreased chelation. On prolong treatment, high molecular weight chitosans may undergo depolymerization due to hydrolysis and may also display more opened conformation due to disentanglement leading to opening up of more sites for chelation, which is more prominent at higher concentration [30,31]. Thus it is the depolymerization leading to opening up of molecular conformation comparatively more prominently in high molecular weight chitosan than in low molecular weight chitosan on prolong treatment and what we virtually see is the reversal in chelation efficiency on prolong treatment.

Effect of particle size of chitosan on chelation of Cu(II) ions

The reduction in particle size of chitosan macromolecule to nano level can furnish increased surface area and hence more number of reactive sites (ligands) for metal scavenging. The particle size of chitosan was reduced by ionotropic gelation with sodium tripolyphosphate (TPP) as described earlier [32]. The varying levels of particle size of nano chitosan, for a given molecular weight chitosan, were obtained by varying the concentration of chitosan. Two different nano chitosans of average particle sizes 408 nm and 534 nm were obtained from CHT from initial concentrations of 1.5 g/L and 2 g/L. These stocks solutions were employed for chelation study of copper ions at concentration 1g/L, obtained by dilution. The effect of particle size on the chelation efficiency of chitosan is shown graphically in Figure 9. The results revealed that the rate of chelation enhanced by the reduction in particle size of chitosan indicating faster establishment of equilibrium with higher equilibrium chelation efficiency. Besides the increased surface area due reduction in particle size, the presence of TPP can also act as a ligands for scavenging the copper ions [29].



Concentration of chelating agent 1g/L, Initial concentration of Cu(II) ions 394.32 mg/L, pH 5.5
Figure 9 Effect of particle size on chelation efficiency of CHT for Cu(II) ions

Conclusion

The presence of excessive copper ions adversely affect the bleaching efficiency and dyeing results. Chitosan of different molecular weights and quaternized derivatives of varying degree of quaternization were employed in the present experiment. The effect of particle size of chitosan on scavenging efficiency was also studied.

The binding of copper ions to chitosan was confirmed by FTIR. The chelation efficiency of trimethyl chitosan (TMCHT) was reduced with increase in the degree of quaternization. Highly acidic pH was not found to be suitable for chelation of metal ions. A milder acidic condition (pH 5.5) showed better results. The sorption of copper ions was increased with increase in the concentration of chitosan/chitosan derivatives. The extent of chelation was found to be high for low molecular weight chitosan when treated for shorter time and decreased with increase in the molecular weight whereas for higher sorption time a reverse trend was noticed. Reduction in particle size of chitosan enhanced both the rate and amount of scavenging metal ions.

References

1. Manivasakam, N., "Water used in textile processing-quality, treatment and analysis", Sakthi Publications, Coimbatore, 1995.
2. Trotmann, E.R., "Textile scouring and bleaching", 1st ed., B.I.Publications, N.Delhi, 1993.
3. Trotman, E.R., "Dyeing and Chemical Technology of Textile Fibres", 6th ed., Charles Griffin and Co Ltd, London, 1984.
4. Karmaker, S.R., "Chemical Technology in the Pre-treatment Processes of Textiles", Science and Technology-12, Elsevier Science B.V., Amsterdam, 1999.
5. Lokhande, R.S., Singare, P.U., and Pimple, D. S., Pollution in Water of Kasardi River Flowing along Taloja Industrial Area of Mumbai, India, *World Environment*, **1**(1) 6-13, (2011).
6. www.cpcb.nic.in
   Groundwater Quality Series:Gwqs/ 10/2007-2008, Status of Groundwater Quality In India -Part-II, Central Pollution Control Board (Ministry of Environment And Forests) **63**, April (2008).
7. Norman, P.I., and Seddon, R., Pollution control in the textile industry - the chemical auxiliary manufacture's role, *J. Soc. Dy. and Col.*, **25**(4), 150-152(1991).
8. Kennedy, M., Electrochemical wastewater treatment technology for textiles, *Am. Dy. Rep.*, **80**(9), 6–29(1991).
9. Landage, S. M., Removal of heavy metals from textile effluent, *Colourage*, **56**(6), 51-56 (2009).
10. Randall, J.M., Garett, V., Bermann, G., and Waiss, A.C., Removal and recycling of heavy metal ions from waste solutions, *Forest Prod. J.*, **24**(9), 80-84 (1974).
11. Suemitsu, R., Uenishi, R., Akashi, I., and Nakano, M., The use of dyestuff-treated rice hulls for removal of heavy metals from waste water, *J. Appl. Polym. Sci.*, **31**(1), 75-83(1986).
12. Randall, J.M., Reuter, F.W., and Waiss, A.C., Removal of cupric ion from solution by contact with peanut skins, *J. Appl. Polym. Sci.*, **19**(6), 1563-1571(1975).
13. Masri, M.S., Reuter, F.W., and Friedman, M., Binding of metal cations by natural substances, *J. Appl.*

Polym. Sci., **18**(3) 675-681(1974).
14. Friedman, M., and Waiss, A.C., Mercury uptake by selected agricultural products and by-products, *Environ. Sci. Technol.*, **6,** 457-458(1972).
15. Inamdar, M.S., and Chattopadhyay, D.P., Chitosan and its versatile applications in textile processing, *Man-Made Textile in India*, **49**(6), 211-216(2006).
16. Alves, N.M. and Mano, J.F., Chitosan derivatives obtained by chemical modifications for biomedical and environmental applications, *Int. J. Bio. Macromol.*, **43**, 401–414 (2008).
17. Jaykumar, R., Prabhaharan, M., Reis, R.L., and Mano, J.F., Graft copolymerization of chitosan- present status and applications, *Carbohyd. Polym*, **62**, 142-158 (2005).
18. Chattopadhyay, D.P. and Inamdar, M.S., Aqueous behaviour of chitosan, *Int. J. Polym. Sci.*, **2010**, 1-7(2010).
19. Karthikeyan, G., Anbalagan, K., and Andal, N. M., Adsorption dynamics and equilibrium studies of Zn (II) onto chitosan, *J. Chem. Sci.*, **116** (2), 119–127(2004).
20. Nomanbhay, S.M. and Palanisamy, K., Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal", *Electron. J. Biotechnol.*, 8(1), 43-53(2005).
21. Chang, Yang-Chuang., and Chen, Dong-Hwang., Recovery of Gold(III) ions by a chitosan coated magnetic nano-adsorbent, *Gold Bull.***, 39**(3), 98-102 (2006).
22. Guibal, E., Vincent, T., and Mendoza, R. N., Synthesis and characterization of a thiourea derivative of chitosan for platinum recovery, *J. Appl. Polym. Sci.*, **75**(1), 119–134(2000)
23. Abdel-Mohdy, F.A., Ibrahim, M.S., and El-Sawy, S., Metal removal by chitosan and some chitosan composites", *J. Text. Asso.***, 66** (5), 219-226(2006).
24. Chattopadhyay, D. P., and Inamdar, M.S., Studies on the properties of chitosan treated cotton fabric, *Asian Dyer*, **5** (6), 47-53(2009).
25. Desai, N.F., "Profiles in Analysis of Chemicals", Gokul Publishers, Mumbai, 1983.
26. Li, P., Dai, Y.-N., Zhang, J.-P., Wang, A.-Q., and Wei, Q., Chitosan–alginate nanoparticles as a novel drug delivery system for nifedipine, *Int. J. Biomed. Sci.*, **4**(3), 221-228 (2008).
27. Avadi, M.R., Amini, G.M., Sadegi, A.M., Irfan, M., Amini, M., Tehrani, M. R., and Shafiee, A., Synthesis and characterization of N- diethyl methyl chitosan, *Iran. Polym. J*. **13**(5), 431-436(2004).
28. Wang, R.-M., He, N.-P., Song, P.-F., He, Y.-F., Ding, L., and Lei, Z.-Q., Preparation of nano-chitosan Schiff-base copper complexes and their anticancer activity, *Polym. Adv. Technol*., **20**, 959–964(2009).
29. Soni, P.L., "Inorganic chemistry", 29th ed., Sultan Chand Sons, N.Delhi, 2007.
30. Vel´asquez, C. L., Albornoz, J. S. and Barrios, E.M., Viscometric studies of chitosan nitrate and chitosan chlorohydrate in acid free NaCl aq solution, *e-Polymers*, no.014, (2008).
31. Hwang, J. K. and Shin, H. H., Rheological properties of chitosan solutions, *Kor. Aust. Rheol. J.*, **12**(3-4), 175–179(2000).
32. Chattopadhyay, D.P., and Inamdar, M.S., Improvement in properties of cotton fabric through synthesized nano-chitosan application, *Indian J. Fibre Text. Res.*, **38**, 14-21(2013).

Indian Journal of Fibre & Textile Research
Vol. 38, March 2013, pp. 14-21

Improvement in properties of cotton fabric through synthesized nano-chitosan application

Debapriya Chattopadhyay[a] & M S Inamdar[b]

Department of Textile Chemistry, Faculty of Technology & Engineering,
The M S University of Baroda, Vadodara 390 001, India

Received 22 January 2012; revised received and accepted 31 May 2012

In this paper, the study on synthesis, characterization and application of nano-chitosan on cotton fabric has been reported. The nano-chitosan treated fabrics are then tested for appearance, tensile, absorbency, stiffness, dyeing behaviour, wrinkle recovery and antibacterial properties. Low molecular weight chitosans are prepared by nitrous acid hydrolysis method; the molecular weights are determined viscometrically. Nano-chitosans are synthesized by ionic gelation of pentasodium tripolyphosphate and chitosan, and then characterized by particle size determination. The fabric samples are pretreated with normal and nano-chitosan solutions by pad-dry-cure technique. The surface morphology of treated cotton fabric has been studied by SEM analysis. The treated fabrics have also been dyed and their whiteness, yellowness and brightness indices are evaluated. It is found that the particle size and polydispersity of chitosan in solution are affected by the variation in molecular weight. The dye uptake and wash fastness of nano-chitosan treated fabrics are found to be improved. An enhanced antibacterial property is observed with the reduction of nano-chitosan particles and when coupled with nano silver colloid.

Keywords: Antibacterial property, Chitosan, Cotton, Dyeing behaviour, Nano-chitosan, Wrinkle recovery

1 Introduction

Various wet processing operations of textiles from initial preparatory processes to final finished clothes are now focused for green technology. Several conventional non-ecofriendly chemicals are being replaced by natural based products that are safe to environment and health during manufacturing and usage. Applications of enzymes in preparatory and in bio-polishing, natural dyes for coloration, biopolymers and their derivatives in fibre production and finishing processes, etc are some of them. One such biopolymer of great interest in recent years is chitosan, derived from alkaline deacetylation of chitin[1].

The precursor chitin is a nitrogen containing polysaccharide, which is second most abundant biopolymer after cellulose; distributed in the shells of crustaceans such as crabs, shrimps and lobsters as well as in the exoskeleton of marine zoo-plankton, including coral, jellyfish and squid pens. It is totally ecofriendly and renewable[2,3].

Chemically, chitosan is a linear (1-4) linked 2- amino-2-deoxy-β- d- glucan (i.e. β- d-glucosamine) having the structure very much close to that of cellulose except the hydroxyl group in C (2) of cellulose is being replaced by amino group in chitosan. Indeed, it is a copolymer of N-acetyl-glucosamine and glucosamine units. Being a primary aliphatic amine, chitosan can be protonated by various acids[1, 2, 4].

By virtue of several valuable inherent properties such as antibacterial, antifungal, antiviral, antacid, non-toxic, total biodegradable, biocompatible with animal and plant tissues as well as film formation, fibre formation and hydrogel formation properties, chitosan has prospective applications in many fields such as biomedical, waste water treatment, cosmetics, dentifrices, food, agriculture, pulp & paper, and textile industries[5-7].

In textiles, the application potential of chitosan is reviewed comprehensively[8,9]. Investigations have shown that it can also be used as a dye fixing agent, for shade and naps coverage, to improve the fastness of dyed fabrics, as a binder in pigment printing, as a thickener in printing. By virtue of its bacteria impeding property, chitosan can prevent garments to develop bad odour[4,10-14]. An improved wrinkle recovery of cotton fabric is reported on finishing cotton with citric acid solution in presence of chitosan with minimum loss in tensile strength due to citric

[a]Corresponding author.
E-mail: dpchat6@gmail.com
[b]Present address: Faculty of Textile Processing, Sarvajanik College of Engineering & Technology, Surat 395 001, India.

acid treatment[15]. It is found that complete inhibition of *Escherichia coli* and Hay bacillus bacteria is possible by treatment of cotton with 0.5gpL chitosan concentration[16]. Tiwari and Gharia[17] attempted to use chitosan as a thickener in printing paste. Performance of the prints with respect to *K/S*, wash fastness, crock fastness and hand are observed to be unsatisfactory. Our earlier investigations[18] have shown improved dyeability towards direct dyes of Chitosan pretreated cotton fabric and the degree of improvement was found to be a function of molecular weight and concentration of chitosan. The fastness to washing of direct dyes on chitosan pretreated fabric, however, was only slightly improved especially for the low molecular weight chitosan applications. Chitosan treated cotton fabric also showed a substantial dyeability towards acid dyes. The appearance and handle of the treated fabric, however, was severely affected. The wrinkle recovery property was found to be reduced. The loss in inherent qualities of cotton fibres due to chitosan may be attributed to the rigid film deposition of it, mostly confined to surface of fibre only.

Today's need, however, is to improve above properties without altering the inherent natural qualities of cotton. It is possible by achieving the maximum penetration of polymer particles into fibre structure and increasing its effectiveness at lowest possible concentration. Penetration of chitosan solution can be improved by lowering the viscosity of its solution, which is obtained by lowering the concentration and/or by reducing the particle size. Reduction in concentration of normal chitosan in solution, however, may reduce its effectiveness and larger chain does not permit its entry into the yarn/cellulose structure. The only possible way is to reduce the particle size, which, in addition to decrease in viscosity, offers greater surface area and hence increase the effectiveness of chitosan. This is the basis of today's most popular technology 'nano technology concept'.

The potential applications of nano-chitosan are well demonstrated in medical field particularly in controlled drug delivery systems[19-21]. However, their applications in textiles are not yet well investigated. The practical application of such nano-chitosan to textiles at shop floor level demands suitable technology for the production of nano-chitosan dispersions, characterization and the analysis of stability of standing baths.

Therefore, in the present work, an attempt has been made to set a simple methodology to produce nano-chitosan by ionotropic gelation with pentasodium tripolyphosphate. Chitosans of different molecular weights are obtained by controlled depolymerisation of parent chitosan using nitrous acid hydrolysis and these products are subsequently used for the synthesis of nano-chitosan. The study reported here is the final results of many basic experiments after getting the confirmation of reproducibility. A representative concentration of 1gpL is, therefore, only reported and discussed here to make it as brief as possible and to avoid presenting less important data. The effect of particle size on various properties of nano-chitosan treated cotton fabric, such as appearance, stiffness, absorbency, dyeing behaviour and wrinkle recovery, is discussed. Scanning electron microphotographs of nano-chitosan treated cotton fabric are also analysed.

2 Materials and Methods

2.1 Materials

100% cotton fabric (count 40s × 40s, EPI 142, PPI 72 and GSM 125), ready for dyeing stage, was procured from local process house.

Direct dyes, namely C.I.Direct Red 81 and C.I.Direct Blue 71, were obtained from M/s Colourtex Industries Ltd, Gujarat State, India. Chitosan (CHT1), having degree of deacetylation (DAC) 90% and viscosity 22cPs, was obtained from M/s Mahtani Chitosan Pvt. Ltd., Gujarat State, India. Dimethylol dihydroxy ethylene urea (DMDHEU) was obtained from local process house and other chemicals such as sodium tripolyphosphate (TPP), acetic acid, sodium nitrite, sodium acetate (anhydrous) and sodium hydroxide used were of analytical grade.

2.2 Synthesis and Characterization of Nano-chitosan

Different molecular weight grades chitosans were first obtained by depolymerization of CHT1 by nitrous acid hydrolysis method, which were employed for the preparation of nano-chitosan dispersions as described elsewhere[22]. In general, chitosan was dissolved in acetic acid solution and optimized quantity of TPP was added drop wise with rapid stirring (about 400 rpm) to obtain an opalescent solution. The sample was allowed to stand overnight, filtered through sintered glass filter of porosity grade G3 and preserved in refrigerator. The prepared nano-chitosan was termed as CHT1N. The synthesized nano-chitosan was applied to cotton fabric within 24 hours since the stability of nano-chitosan gets adversely affected with time as discussed earlier [22]. The specifications of different grades of chitosan and nano-chitosan are given in Table 1. The particle size and size distribution of the chitosan were analyzed on

Table 1—Particle size of nano-chitosan as a function of molecular weight

[CHT:TPP:: 1:0.15]

Parent chitosan		Synthesized nano-chitosan	
Sample code	Molecular weight	Sample code	Particle size nm
CHT1	135,839	CHT1N(i)[a]	468.1
		CHT1N(ii)[b]	319.4
CHT2	71,676	CHT2N	271.6
CHT3	38,733	CHT3N	231
CHT4	20,698	CHT4N	195.2
CHT5	11,986	CHT5N	110.74

[a]Obtained by dilution of CHT1N of 2 gpL concentration to 1gpL.
[b]Synthesized directly from CHT1 of 1 gpL concentration.

the particle size analyzer (Model: Zetasizer Nano ZS90, Make: Malvern Instruments Ltd, UK).

2.3 Treatment of Fabric with Nano-chitosan

Nano-chitosan dispersion (1gpL) was applied onto fabric on a padding mangle with wet pick-up of 70% by two dip- two nip method. After drying the fabric was cured in oven at 150 ^{0}C for 4 min. The sample was then washed in the following sequence**:** rinse → alkali wash (soda ash 1 gpL, MLR 1:50) → hot wash (twice) (85 ^{0}C / 20min) → cold wash → dry.

2.4 Test Methods

SEM Study

Treated and untreated fabric samples were fixed on carbon coated aluminium sheets and then were observed under scanning electron microscope (Model JSM5610LV, version 1.0. Joel, Japan) in vacuum.

Evaluation of Indices

The samples were evaluated on Spectroscan 5100A (Make: Premier Colorscan) for whiteness index (10 deg / D65 / Hunterlab), yellowness index (2 deg / C/ ASTM D 1925), brightness index (2 deg / C / TAPPI 452 / ISO 2470).

Fabric Stiffness, Tenacity and Absorbency

Stiffness in terms of bending length was measured as per standard ASTM D 1388-996. The tenacity and elongation-at-break of treated and untreated cotton fibres were measured on Stelometer (Make: Eureka Precision Instrument & Co., Coimbatore, India). The breaking load (kg) and elongation-at-break were obtained directly from scale. The samples were then collected and weighed. An average of 5 readings was calculated using following formula:

$$\text{Tenacity (g/tex)} = \frac{\text{Breaking load (kg)} \times 1.5 \times 10}{\text{Sample weight (mg)}}$$

Sample length = 1.5 cm

Absorbency of treated and untreated cotton fabrics was evaluated as per AATCC test method 79-2000.

Fabric Dyeing

The fabric sample was immersed in dye bath maintained at material-to-liquor ratio of 1:40 and containing 1% direct dye, Glauber's salt (20% owf) and soda ash (5% owf). The sample was run in the bath for 15 min at room temperature. Temperature was then raised to 90 ^{0}C and dyeing was continued for 60 min. The dyed sample was then rinsed with cold water 3 times, air dried and hot pressed.

In case of nano-chitosan pretreated material the dyeability was also checked after making the dye bath slightly acidic using 0.5 gpL acetic acid after completion of conventional dyeing process. Presence of acid protonate the amino group which enhances further absorption of dyes.

The dyed samples were evaluated for colour strength in terms of *K/S* values on Premier Colorscan (India) make computer colour matching system namely Spectroscan 5100A. The wash fastness of dyed samples was evaluated according to ISO 1.

Crease Recovery Angle and Antimicrobial Activity

Crease recovery angles were measured as per AATCC test method 66-2003.The untreated and treated samples were subjected to soil burial test as per AATCC Test Method 30-2004. After the stipulated period the samples were removed, washed with water and dried in air. The samples were then tested for strength measurement on stelometer.

3 Results and Discussion

3.1 Synthesis and Characterization of Nano-chitosan

Chitosan has fairly long linear structure with rigid conformation. The characteristic size of CHT1 hydrodynamic sphere is found to be 4014 nm. Such a higher particle size offers higher viscosity to the solution. It is possible, for a given molecular size chitosan, to reduce the particle size to nano level by 'bottom-up' approach[23]. Chitosan, by virtue of polycationic nature, undergoes ionic gelationwith polyanions such as pentasodium tripolyphosphate (TPP), ethylene diamine tetra acetic acid (EDTA), etc to form nano-particles. Such particles are stabilized by electrostatic hindrance due to coulombic repulsion between particles of same ionic charges[24-26]. Owing to faster

ionic reactions between chitosan and TPP, non-toxic nature of these components[23] and ease of operation, we adopted the gel ionization technique for the synthesis of nano-chitosan particles. The particle size distribution of CHT5N, having particle size 110.74nm, is given in Fig.1. Scaling down the particle size of large polymeric materials to nano level is a big challengeIt is clear from the present study that the molecular weight (Table 1) has a great role in controlling the particle size and by reducing the molecular weight we achieved about 110 nm particle size. It is clear from this investigation that the particle size can be reduced below 100 nm by experimenting with parent chitosan of low molecular weight (lower than 10,000). We believe that the study would act as a platform for further work of this kind and would serve basic information to the future researchers.

3.2 Effect of Nano-chitosan Application on Surface Morphology

The surface morphology of the treated and untreated cotton was studied under scanning electron microscope (Fig. 2). Chitosan exhibits an inherent property of film formation, which is clearly seen as

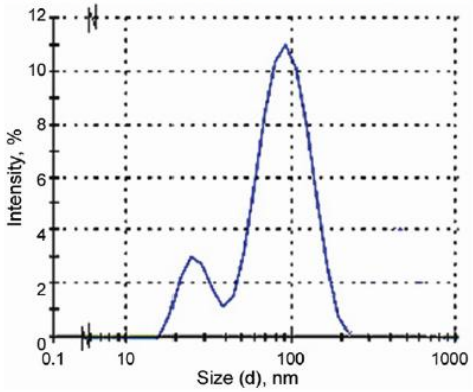


Fig. 1—Size distribution of nano-chitosan by intensity (CHT5N)

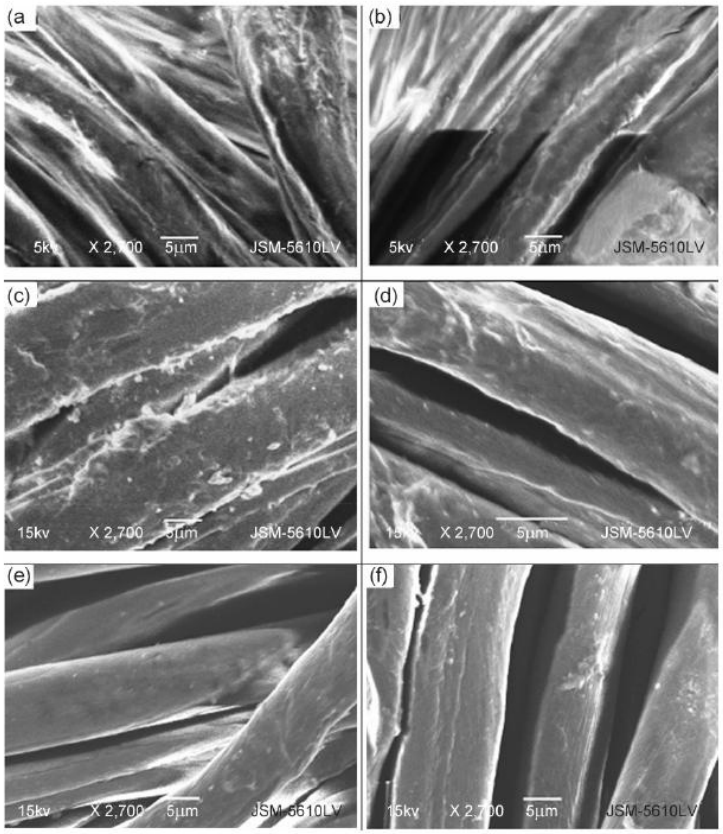


Fig. 2—Scanning electron microphotographs (×2700) of (a) cotton Fibre (control), (b) CHT1 treated fibres, (c) CHT1 treated and then prolong boiled cotton fibres, (d) CHT1N(ii) 319.4nm, treated cotton fibres, (e) CHT4N, 195.2nm, treated cotton fibres and (f) CHT5N,110.74nm, treated cotton fibres

gloss on fibre surface as shown in Fig 2(b). Further, the film deposition on fibre surface can be confirmed by prolong boiling of treated sample in distilled water so that the broken appearance of film can be viewed under SEM [Fig. 2(c)]. Nano-chitosan treated samples show all together different microphotograph [Figs 2(d) – (f)]. Nano-chitosan film is found to be more uniform.

3.3 Effect of Nano-chitosan on Fabric Appearance

The appeal of the fabric is manifested by its appearance and the feel. Effect of particle size of nano-chitosan on these properties of cotton fabric is illustrated in Table 2.

The appearance and the fabric feel are quite satisfactory. It is envisaged from Table 2 that the whiteness is improved with reduction in particle size and reaches well nearer to that of control sample. This may be attributed to the greater extent of penetration of nano-chitosan particles into fibre structure and allowing the cuticle for exposure. Deposition of normal chitosan, however, is confined to surface as a film, which alters the whiteness to some extent. This film may also impart stiffness to the fibre, whereas a nano-chitosan shows a little influence, as is observed in same table.

3.4 Effect of Nano-chitosan on Tensile Properties

The effect of nano-chitosan treatment on tensile properties of cotton fabrics is presented in Table 3.

There is a reduction in strength due to conventional chitosan application. Conventional chitosan mostly forms a film on the surface of the fabric and very less amount of it can enter in to the inter-fibre regions, thus cannot take part in load bearing phenomenon, rather affects symmetrical distribution of load. Nano-chitosan, on the other hand, because of its small size can easily enter into the inter-fibre region and to even inter-cellulosic chain regions, and work as a cross-link which bears the load to a great extent. The strength improvement is therefore clearly observed with the reduction in particle size. The elongation property is, however, decreased to some extent with the scaling down of particle size. The formation of *in situ* three dimensional networks probably resists the adjacent fibre molecules to slip and lowers the elongation-at-break.

3.5 Effect of Nano-chitosan on Absorbency

The absorbency, measured by drop penetration method, of nano-chitosan treated cotton fabric is shown in Fig. 3. The results show that the absorbency is decreased with the reduction in particle size. This may be elucidated by the example of lotus leaf effect. Distribution of nano-chitosan particles as a thin layer over and beneath the surface, [Fig. 2 (d)-(f)], may roll out the water droplets. Nevertheless, the absorbency of nano-chitosan treated samples is still within the tolerable limits of conventional wet processing conditions.

3.6 Dyeing Behaviour of Nano-chitosan Treated Cotton Fabric

Since the structure of chitosan is very much similar to cellulose, it is anticipated that its treatment to cotton should influence the dyeing. Hence, the effect of pretreatment of nano-chitosan on direct dyeing of cotton has been studied. The effects of chitosan and nano-chitosan pretreatment on dye uptake are shown in Table 4. The dye uptake by treated cotton fabric, in conventional process, is increased progressively with reduction in particle size of CHTN. The results are superior to corresponding parent CHT treated materials. The dye uptake of CHTN treated samples is found to be significantly increased, resulting in almost complete exhaustion of dye bath, when acidification was followed. The increased dye uptake due to chitosan treatment may be attributed to the presence of primary amino groups of chitosan. These cations

Table 2—Effect of particle size of nano-chitosan on appearance and stiffness of cotton fabric

Sample code	Particle size nm	Appearance			Bending length, cm	
		W.I.	Y.I.	B.I.	Warp	Weft
Control	-	92.5	2.6	84.6	2.05	1.68
CHT1	4014	90.9	4.9	81.8	2.44	1.70
CHT1N(i)	468.1	91.1	4.6	82.4	2.29	1.71
CHT1N(ii)	319.4	91.1	4.6	82.3	2.26	1.70
CHT2N	271.6	91.5	3.6	83.4	2.24	1.70
CHT3N	231.0	92.1	3.2	83.7	2.24	1.71
CHT4N	195.2	91.9	3.4	83.8	2.21	1.70
CHT5N	110.74	92.1	3.2	83.8	2.19	1.70

W.I.—Whiteness index, Y.I.—Yellowness index, B.I.—Brightness index.

dissipate the negative surface charge on cotton and drives dye molecules to the fibre. Further, the dye uptake may also been enhanced due to the dyeability of chitosan itself with direct dyes. The nano-chitosan due to increased surface area and hence higher accessibility for dye sites put much added value. The primary amino groups on chitosan get protonated (quaternized) in acidic medium having enhanced positive charge, thus form salt linkages with anionic (sulphonate) groups of residual dye in the bath. Secondly, the higher dye uptake value after acidification proves the presence of chitosan.

The wash fastness and rub fastness properties of direct dyed fabrics were also analyzed, which are presented in Table 5. The fastness to washing is improved with the reduction in particle size. This may be regarded to the formation of CHTN-dye complex *in situ*. The fastness to rubbing is also improved to some extent with the reduction in particle size.

Table 3—Effect of nano-chitosan on tensile properties of cotton fabric
[Control cotton fabric: Tenacity = 23.33 g/tex, Elongation-at-break=5.25%]

Parent chitosan			Nano-chitosan		
Sample code	Tenacity g/tex	Elongation-at-break, %	Sample code	Tenacity g/tex	Elongation-at-break, %
CHT1	20.48	4.75	CHT1N(i)	23.48	4.5
			CHT1N(ii)	25.17	4
CHT2	21.01	4.5	CHT2N	25.61	4
CHT3	21.45	4.5	CHT3N	25.56	4
CHT4	22.19	4.25	CHT4N	25.71	3.75
CHT5	21.81	4.5	CHT5N	25.72	3.5

3.7 Effect of Nano-chitosan on Crease Recovery

The proneness to creasing downgrades the aesthetic appeal of cotton cloth or garments. This problem of cotton fabric is conventionally overcome by the treatment with various cross-linking agents based on

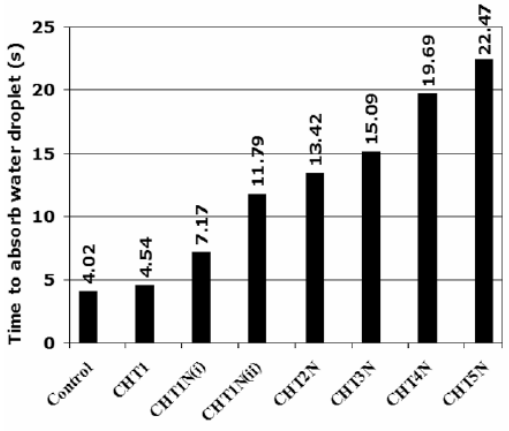


Fig. 3—Effect of particle size on absorbency of treated cotton fabric

Table 4—Effect of particle size of nano-chitosan on dye uptake of treated cotton fabric

Parent chitosan			Nano-chitosan				
Sample code	*K/S* (Conventional dye bath)		Sample code	*K/S*[a]			
				C. I. Direct Red 81		C. I. Direct Blue 71	
				Conventional dye bath	Acidic dye bath	Conventional dye bath	Acidic dye bath
CHT1	9.0	6.9	CHT1N(i)	9.6 (24)	10.2 (62)	7.2 (19)	8.0 (63)
			CHT1N(ii)	9.6 (24)	10.4 (64)	7.4 (22)	8.1 (63)
CHT2	9.0	7.0	CHT2N	9.8 (27)	10.5 (66)	7.4 (22)	8.2 (66)
CHT3	9.0	6.8	CHT3N	9.8 (27)	10.5 (66)	7.7 (26)	8.2 (66)
CHT4	9.0	6.7	CHT4N	9.8 (27)	10.5 (66)	7.8 (28)	8.2 (66)
CHT5	9.1	7.1	CHT5N	9.9 (29)	10.6 (67)	7.8 (28)	8.4 (69)

[a]Values in parentheses indicate per cent improvement in *K/S* as compared to corresponding control fabric sample.
C. I. Direct Red 81— *K/S* values of controlled cotton fabric dyed in conventional dye bath is 7.7 and in acidic dye bath it is 6.3.
C. I. Direct Blue 71— *K/S* values of controlled cotton fabric dyed in conventional dye bath is 6.1 and in acidic dye bath it is 4.9.

Table 5—Effect of particle size on fastness properties of direct dyes (conventional dye bath)

Sample code	Particle size nm	C. I. Direct Red 81		C. I. Direct Blue 71	
		Wash fastness	Rub fastness	Wash fastness	Rub fastness
Control	-	3	2-3	4	2-3
CHT1	4014	3	2	4	2
CHT1N(i)	468.1	3-4	2-3	4-5	2
CHT1N(ii)	319.4	3-4	2-3	4-5	2-3
CHT2N	271.6	3-4	2-3	4-5	2-3
CHT3N	231.0	4	2-3	4-5	2-3
CHT4N	195.2	4	2-3	5	3
CHT5N	110.7	4-5	3	5	3

Table 6—Effect of particle size of nano-chitosan on wrinkle recovery property of cotton fabric

Sample code	Pad bath concentration gpL	Particle size nm	Crease recovery angle Â
Control	-	-	161
DMDHEU (40%)	20	-	180
	40	-	207
	60	-	215
CHT1	1	4014	144
CHT1N (i)	1	468.1	158
CHT1N(ii)	1	319.4	162
CHT2N	1	271.6	162
CHT3N	1	231.0	163
CHT4N	1	195.2	165
CHT5N	1	110.7	170

aminoplast resins, e.g. DMDHEU[29]. The crease recovery property as a function of chitosan and nano-chitosan treatments has been compared against DMDHEU (Table 6). The crease recovery angle of cotton fabric is greatly reduced by the treatment of normal chitosan (CHT1). Treatment of cotton fabric with chitosan of lower particle size is found to improve the crease recovery of cotton fabric (Table 6). However yet it could not gain the rating of commercially used cross-linking agent DMDHEU. Conventional chitosan is believed to form a surface coating which lowers the possibility of cross-linking and therefore cannot contribute to the load sharing phenomenon. The improved wrinkle recovery property in case of nano-chitosan treatment may be attributed to the greater penetration into fabric structure. These polycationic nano-particles, due to better penetration, may bound the fibre molecules and resist creasing to some extent.

Table 7—Effect of nano-chitosan treatment on resistance towards microbial attack

Sample code	Tenacity, g/tex		Change in strength from untreated cotton fabric[a], %
	Before soil burial	After soil burial	
Control	23.33	18.98	-18.65
Cotton[b] (Blank treated)	20.87	18.08	-22.5
CHT1	20.48	19.47	-16.55
Ag nano	22.68	22.20	-4.84
CHT1+ Ag nano	24.51	20.27	-13.10
CHT1N(ii)	25.17	21.84	-6.39
CHT1N(ii)+Ag nano	24.21	22.94	-1.67
CHT5N	25.72	22.38	-4.07
CHT5N+Ag nano	25.67	23.03	-1.29

[a]-ve sign indicates the loss in strength.

[b]Cotton (blank treated): Acetic acid (15 gpL) applied by pad-dry-cure method.

3.8 Effect of Nano-chitosan on Antibacterial Effect

Cotton fibres like other natural fibres provide favourable environment for the growth of microorganisms due to moisture and warmth. These organisms are mainly responsible for discolouration, development of rancid/bad odour, stains and strength loss of fabric as well as skin allergies and infection diseases to human body[8,27]. One of the most popular ways of imparting antimicrobial resistance is to use nano-silver colloid. Chitosan, being polycationic material, binds to anionic surfaces of microbe cell wall and disrupt it leading to death of cell[9]. Attributing to the antibacterial and metal particle retention properties of chitosan[28], the fabric was treated with chitosan and nano-chitosan and then with nano silver colloid. Nano-silver colloid of concentration $1 \cdot 10^{-3}$ M /100 mL and average particle size 110nm was prepared as published elsewhere[30].

The resistance against bacterial attack of untreated and treated samples of cotton was determined by measuring the loss in strength due to soil burial test. The results are presented in Table 7. It can be observed that the chitosan can be employed as an efficient antibacterial agent. The effect is enhanced with the reduction in particle size of nano-chitosan and coupling with nano-silver.

4 Conclusion

Ionotropic gelation with pentasodium tripolyphosphate is employed for the preparation of

nano-chitosan dispersion. From the stand point application of nano-chitosan to cotton fabric, following conclusions can be drawn.

4.1 The appearance and handle of nano-chitosan treated cotton fabric is quite satisfactory.

4.2 Nano-chitosan treatment shows improvement in fibre strength that increases with the reduction in particle size. The elongation-to-break is slightly decreased with the scaling down of particle size.

4.3 Moisture related property such as absorbency is affected; nevertheless it is in acceptable limit of tolerance.

4.4 The dyeability of chitosan and nano-chitosan treated cotton a fabric towards direct dyes is improved significantly. The progress is sustained with reduction in particle size. The effect is further enhanced after acidification of dye bath. Fastness to washing is improved satisfactorily and fastness to rubbing slightly.

4.5 Wrinkle recovery property is slightly improved and use of suitable cross-linking agent is essential.

4.6 Nano-chitosan together with nano-silver treatment shows enhanced antibacterial activity.

References

1 Muzzarelli R A A, in *The Polymeric Materials Encyclopedia,* edited by J C Salamone (CRC press Inc.,Boca Raton Fl, USA), 1996, 312.

2 Hirano S, *Ullmann's Encyclopedia of Industrial Chemistry,* Vol.7 (Wiely-VCH, Weinheim, Germany), 2003, 679.

3 No H K & Meyers S P, *J Aquatic Food Product Technol*, 4 (1995) 27.

4 Oktem T, *Color Technol,* 119 (2003) 241.

5 Harish Prashant K V & Tharanathan R N, *Trends Food Sci Technol,* 18 (2007) 117.

6 Giri Dev V R, Neelkandan R, Sudha N, Shamugasundaram O L & Nadaraj R N, *Text Magazine,* July (2005) 83.

7 Kean T, Roth S & Thanou M, *J Control Rel,* 103 (3) (2005) 643.

8 Daniela Enescu, *Roumanian Biotech Letters,* 13 (6) (2008) 4037.

9 Inamdar M S & Chattopadhyay D P, *Man Made Text India,* 49 (6) (2006) 212.

10 Achwal W B, *Colourage,* 47 (9) (2000) 47.

11 Achwal W B, *Colourage*, 50 (8) Aug (2003) 51.

12 Hasebe Y, *AATCC Rev*, 1(11) (2001) 23.

13 Eom S I, *AATCC Rev*, 1(3) (2001) 57.

14 Knittel D & Schollmeyer E, *Melliand English,* (1-2) (2002) E 15.

15 Tahlawy Kh F El, *Colourage*, 46 (5) (1999) 21.

16 Zhang Z, Chen L, Ji J, Huang V & Chen D, *Text Res J*, 73 (12) (2003) 1103.

17 Tiwari S K & Gharia M M, *AATCC Rev*, 3(4) (2003) 17.

18 Chattopadhyay D P & Inamdar M S, *Asian Dyer*, 5 (6) (2009) 47.

19 Patel J K & Jivani N P, *Int J Pharm Sci Nanotech*, 2(2) (2009) 517.

20 Hong-liang Zhang, Si-huiWu, Yi Tao, Lin-quan Zang & Zheng-quan Su, *J Nanomaterials*, 2010 (2010) 1.

21 Trapani A, Sitterberg J, Bakowsky U & Kissel T, *Intl J Pharm.,* 375 (2009) 97.

22 Chattopadhyay D P & Inamdar M S, *Int J Polym Sci*, 2010 (2010)1.

23 Lopez-Leon T, Carvalho E L S, Seijo B, Ortega-Vinuesa J L & Bastos-Gonzalez D, *J Coll Interface Sci*, 283 (2005) 344.

24 Boonyo W, Junginger H E, Waranuch N, Polnok A & Pitaksuteepong T, *J Met Mat Min,* 18(2) (2008) 59.

25 Loretz B & Bernkop–Schnürch, *AAPS J,* 8(4) (art. no. 85) (2006) 756-764.

26 Kuo-Shien Huang, Yea-Ru Sheu & In-Chun Chao, *Polymer-Plastics Technol Eng*, 48 (2009) 1239.

27 Gao Y & Cranston R, *Text Res J*, 78(1) (2008) 60.

28 Wen-Li Du, Shan-Shan Niu, Ying-Lei Xu, Zi-Rong Xu & Cheng-Li Fan, *Carbohydr Polym*, 75 (2009) 385.

29 Schindler W D and Hauser P J, in *Chemical Finishing of Textiles* (Woodhead Publishing Limited, Cambridge, England), 2004, 51.

30 Chattopadhyay D P & Patel B H, *Indian J Fibre Text Res*, 34 (2009) 368.

Research Journal of Engineering Sciences ISSN 2278 – 9472
Vol. 1(4), 9-15, October (2012) *Res. J. Engineering Sci.*

Studies on Synthesis, Characterization and Viscosity Behaviour of Nano Chitosan

Chattopadhyay D.P.[1]* and Inamdar M.S.[2]
[1]Department of Textile Chemistry, Faculty of Technology and Engineering, The M.S.University of Baroda, Vadodara-390001, INDIA
[2]Faculty of Textile Processing, Sarvajanik College of Engineering and Technology, Surat-395001, INDIA

Available online at: www.isca.in
Received 25th September 2012, revised 1st October 2012 , accepted 4th October 2012

Abstract

The enhanced performance of chitosan (CHT) treated cotton fabric is anticipated tobe achieved by scaling down the particle size of former to nano level for its greater penetration into the fabric structure. Nano-chitosan (CHTN) was synthesized by ionic gelation of CHT and sodium tripolyphosphate (TPP). The sample was characterized by the determination of particle size and polydispersity index (pdi) on particle size analyzer. Effect of various parameters such as molecular weight and concentration of CHT, concentrations of TPP on particle size were studied. Low molecular weight chitosans were prepared by nitrous acid hydrolysis method and the molecular weights were determined viscometrically. Attempts were made to correlate the viscosity behaviour with particle size of chitosan. The storage stability of CHTN dispersions was studied by periodic evaluation of their viscosity.

Keywords: Chitosan, nano-chitosan, characterization, viscosity behaviour, storage stability.

Introduction

The biopolymer based cationic polysaccharide, chitosan, is obtained by alkaline deacetylation of chitin which is widely distributed in shells of crustacean like lobsters, shrimps, crabs etc. Chemically, chitosan is a linear (1-4) linked 2- amino-2-deoxy-β- d- glucan (i.e. β- d-glucosamine) having the structure very much close to that of cellulose except the hydroxyl group in C (2) of cellulose is being replaced by amino group in chitosan. Indeed, it is a copolymer of N-acetyl-glucosamine and glucosamine units[1-3].

The potential use of chitosan in textiles and various allied fields has attracted strong interest for the development of its several derivatives and colloidal particles of nano level[4-8]. This has been attributed to its valuable inherent properties such as antibacterial, antifungal, antiviral, antacid, non toxic, total biodegradable, biocompatible with animal and plant tissues as well as film formation, fiber formation, hydrogel formation. It is totally eco friendly and renewable[2,9]. Macromolecular chitosan, however, encounters several challenges while its applications to textiles, in particular. Investigations have shown that the inherent properties of cotton fabric such as appearance and handle and other essential properties like fastness of dyes to various agencies due normal chitosan treatment were found tobe affected[10]. These detrimental effects of chitosan are mainly attributed to its lack of penetration into fabric structure causing the surface deposition of film [11,12]. One possible way to enhance its effectiveness is to reduce the particle size closer to nano level, which facilitates the greater penetration of CHT into fabric structure.

The applications of nano chitosan are well demonstrated in medical field particularly as controlled drug delivery systems[13-16]and water treatment for removal of heavy metals[17] and highly pollutant organic compounds like alkyl phenols[18]. However, very few applications nano chitosan in textiles are addressed. Lee et al[19] obtained chitosan and PVA-Chitosan blended submicroscopic fibres by electro spinning method having the average diameter of 200-400 nm. Nano chitosan can be loaded with metal ions such as Ag, Cu, Zn etc to enhance its antibacterial property, as reported by Du et al[20]. The practical applications of nano chitosan to textiles at shop floor level needs suitable technology for its productions, characterization and the analysis of its stability in standing baths. The present work was, therefore, aimed at finding out a simple method of synthesising nano chitosan by ionotropic gelation with sodium tripolyphosphate (TPP) and with the objective to its applications to cotton textiles. The characterization was done by the determination of particle size and polydispersity index (pdi) on particle size analyzer. Chitosans of different molecular weights, obtained by controlled depolymerisation of parent chitosan with nitrous acid hydrolysis, were used for the synthesis of nano particles. The effects of particle size on the viscosity behaviour and the storage stability of their sols are reported.

Material and Methods

Materials: Chitosan (CHT1), having DAC value 90% and viscosity 22cPs, was kindly supplied by M/s Mahtani Chitosan Pvt. Ltd., Gujarat State, India. Other chemicals used such as sodium tripolyphosphate (TPP), acetic acid, sodium acetate (anhydrous), methanol, sodium hydroxide etc were of analytical grade of reputed brands.

Synthesis of low molecular weight chitosan: Different molecular weight grades chitosans were obtained by depolymerization of CHT1 by nitrous acid hydrolysis method as described elsewhere[21]. In general, a 2 % solution of chitosan in acetic acid was prepared. Predissolved dilute solution of sodium nitrite was then added gradually to chitosan solution and stirred for two hrs at 30°C to get desired viscosity level. The depolymerised chitosan was then precipitated out by caustic solution and washed to neutral pH. The precipitates of chitosan was then washed thrice with methanol and dried at 60°C. The molecular weights of these samples were determined viscometrically[22].

Synthesis of nano-chitosan and its characterization: Nano-chitosan dispersions were obtained as described elsewhere[21]. However in general, chitosan (CHT1) was dissolved in acetic acid solution and optimized quantity of TPP was added drop wise with rapid stirring (about 400 rpm) to obtain an opalescent solution. The sample was allowed to stand overnight and filtered through sintered glass filter of porosity grade G3 and preserved in refrigerator. The prepared nano-chitosan was nomenclatured as CHT1N.

The particle size and size distribution of the chitosan were analyzed on the particle size analyzer (Model: Zetasizer Nano ZS90, Make: Malvern Instruments Ltd, UK).

Determination of viscosity: The viscosity behaviour of chitosan solution and nano-chitosan sols were studied using Ubbelohde capillary viscometer (No 1A) at 30°C having flow time for distilled water, T_0=15.57 seconds.

Results and discussion

Synthesis and characterization of nano chitosan: Chitosan has fairly long linear structure with rigid conformation. These long molecules in solid state are, mostly, in the form of tightly folded random coils. Individual molecular coils are also not discrete and separate but are interpenetrating and entangled with each other. In solution, the solvent gradually diffuse into the polymer aggregates resulting into the swelling of the polymer. As swelling continues, the segments of the polymer are solvated and loosened out as bunches of entangled molecules, known as 'hydrodynamic' sphere or ellipsoid[23-25]. The characteristic size of CHT1 hydrodynamic sphere, in our case, at 1 gpl concentration was determined to be 4014 nm. Such higher particle size offer higher viscosity to the solution. It is possible, for a given molecular size chitosan, to reduce the particle size to nano level by 'bottom-up' approach as a result of a self assembling or cross linking processes in which the molecules arrange themselves in to ordered nano scale structure either by physical or covalent inter- or intramolecular interactions[26]. By virtue of primary amino groups, chitosan under goes Schiff's base formation with aldehydes such as glutaraldehyde, salicylaldehyde etc giving chemically cross linked leading to a quite stable matrixes of nano chitosan[14,26,27]. In another kind of reaction, chitosan hydrogels are obtained by ionic gelation, where nano particles are formed by means of electrostatic interactions with polyanions such as pentasodium tripolyphosphate (TPP), ethylene diamine tetra acetic acid (EDTA) etc. Such particles are stabilized by electrostatic hindrance due to coulombic repulsion between particles of same ionic charges[29-31]. Several other methods of synthesis of nano chitosan such as desolvation method, emulsion-droplet coalescence method, reverse micellar method, self-assembly via chemical modification, spray drying[13,14], and nonaqueous electrochemical method[32] are described in liturature. Owing to faster ionic reactions between chitosan and TPP, non toxic nature of these components[26] and ease of operation, we adopted the gel ionization technique for the synthesis of nano chitosan particles. The intramolecular cross linking in chitosan molecule by gel ionization is schematically illustrated in figure 1. The particle size distributions of various samples of CHTN are presented in figure 3.

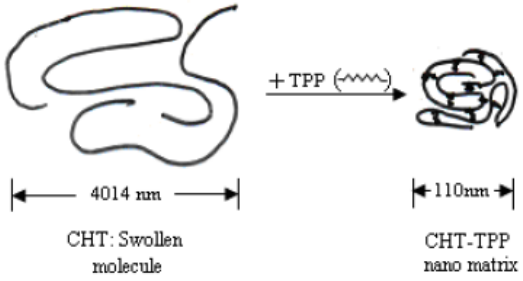


Figure-1
Ionic cross linking of chitosan

Effect of molecular weight of chitosan on particle size: Various grades of low molecular chitosan were produced by controlled depolymerization of high molecular weight one, namely CHT1. When chitosan solution is treated with nitrous acid, produced from acidic solution of sodium nitrite, it undergoes deamination reaction with subsequent cleavage of β-glycosidic linkages[33]. The IR spectra of chitosan and depolymerised chitosan of different molecular weights determined in earlier study[21] were found tobe almost similar indicating that the process of depolymerisation caused no significant chemical changes in their structures. These low molecular weight chitosan derivatives were employed for the synthesis of nano chitosan dispersions.

The influence of molecular weight of chitosan on particle size is presented in table 1 and the graphical correlation between intrinsic viscosity, a function of molecular weight, and particle size of nano chitosan is shown in figure 2. These data illustrate that, under a given condition of concentrations of CHT and TPP, with decrease in molecular weight, the particle size also decreased progressively and followed a curvilinear relation. It is well documented[23, 29] that the higher the molecular weight or the

larger the molecular size, comparatively larger will be the nanomatrix and vise-versa. This relation of particle size with molecular weight in a definite condition of parameters may be useful for synthesis of nano chitosan of desired particle size.

Table-1
Effect of molecular weight on particle size

Parent Chitosan		Synthesized nano chitosan	
Sample Code	Molecular Weight, Mv	Sample Code	Particle size (nm)
CHT1	135,839	CHT1N	319.4
CHT2	71,676	CHT2N	271.6
CHT3	38,733	CHT3N	231
CHT4	20,698	CHT4N	195.2
CHT5	11,986	CHT5N	110.74

CHT:TPP:: 1:0.15

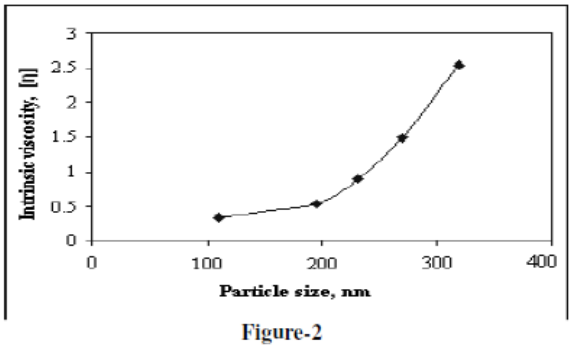


Figure-2
Particle size of chitosan as a function of intrinsic viscosity

Effect of concentration of chitosan on particle size: Two methods were employed for the synthesis of different concentrations of CHTN dispersions namely direct preparation method and dilution method. In first i.e. direct preparation method, the dispersions of nano chitosan from CHT1 of different concentrations such as 0.25, 0.50, 1.0 gpl etc were prepared separately and in the latter, higher concentration nano chitosan dispersion (2 gpl) was prepared first and then diluted to the required concentration with rapid stirring. The effects of these two methods on particle size are presented in table 2. It was observed that at higher concentration, in both the cases; the particle size of CHTN was comparatively large and progressively reduced with the lowering of concentration. The former method, however, was more effective in scaling down the particle size. The larger size of CHTN at higher concentrations may be due overlapping and intermolecular cross linking through TPP bridging resulting into aggregation of polymer molecules. Intramolecular cross linkages in polymer molecule due to TPP at low concentrations, on the other hand, are likely tobe favored for lower particle size. This table also manifests that the poly dispersity indices (pdi) of direct prepared samples were comparatively lower and independent while in dilution method the values were higher and seemed to follow the starting material. The particle size distribution curves, as illustrated in figure 3, were broader for higher concentration samples and became narrow for lower concentration samples. Further, these bands were comparatively narrow for directly prepared samples indicating the uniform size distribution and are close agreement with their lower pdi values.

Effect of TPP concentration on particle size: In ionic gelation reaction, TPP a major ingredient for cross linking has a pronounced effect on the properties of CHTN dispersion. It was observed that with increase in the concentration of TPP the appearance of the system changed from clear viscous liquid to opalescent fluid and then precipitated. The effect of TPP concentration on the particle size is demontrated in figure 4. At concentration of TPP below 0.05 g, very few phosphate ions were present to produce effective ionic linkages with chitosan amino groups; hence, the solution was clear. As the concentration of TPP was increased gradually, the solution became opalescent indicating the formation of nano chitosan. It was revealed from the same figure that with increase in concentration of TPP, the particle size of CHT1-TPP nanomatrix decreased, reached to minimum at about 0.25 g of TPP and then increased. Concentration of TPP above 0.30 g resulted precipitation. The precipitation at excessively higher concentration of TPP may be attributed to the aggregation of chitosan molecules due to excessive cross linking through TPP bridging. Similar trend in terms of viscosity was noticed when the relative viscosity was plotted against TPP concentration, figure 5.

Table-2
Effect of preparation method and concentration of chitosan on particle size

Direct preparation method			Dilution method		
CHT1 (gpl)	Particle size (nm)	Poly dispersity index (pdi)	CHT1N (gpl)	Particle size (nm)	Poly dispersity index (pdi)
0.25	304	0.421	0.25	347.3	0.465
0.50	313.5	0.441	0.50	354.9	0.471
1.00	319.4	0.422	1.00	468.1	0.515
1.50	408.73	0.441	1.50	516.43	0.515
2.00	534.2	0.515	-	-	-

(CHT1: TPP :: 1:0.15)

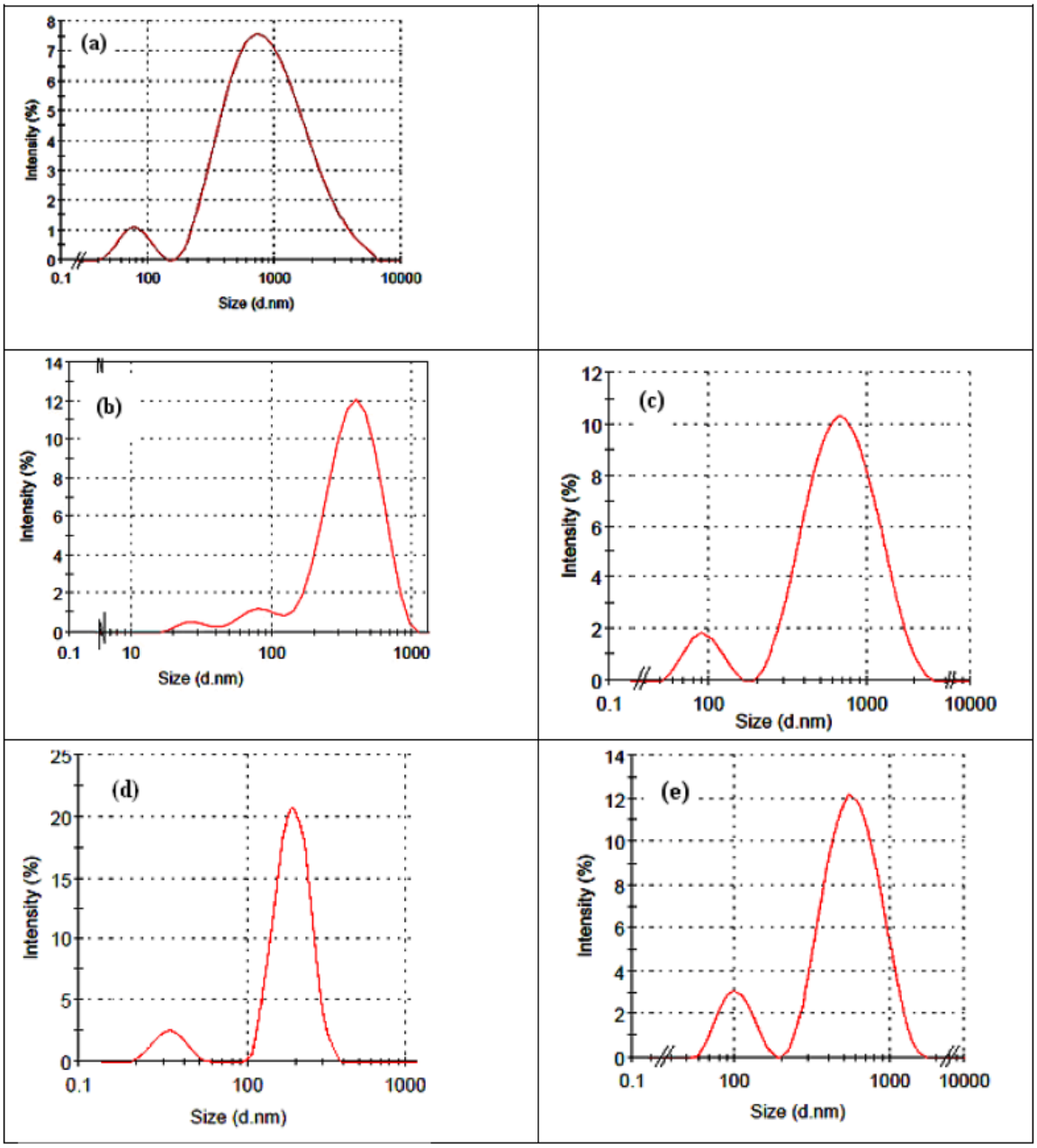


Figure-3
Particle size distribution of nano chitosan as a function of preparation methods: (a)Direct Method: 2gpl (534.2nm), (b) Direct Method: 1gpl (319.4nm), (c) Dilution Method: 1gpl (468.1 nm), (d) Direct Method: 0.5gpl (313.5nm), (e) Dilution Method: 0.5gpl (354.9 nm)

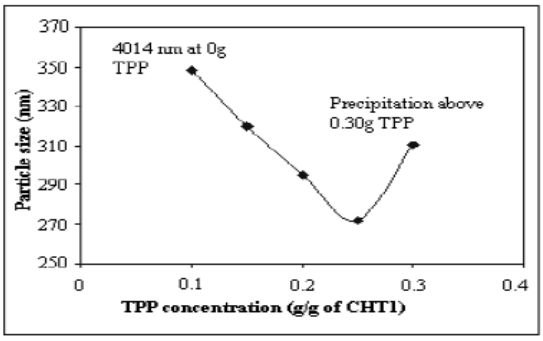


Figure-4
Effect of TPP concentration on particle size of CHT1

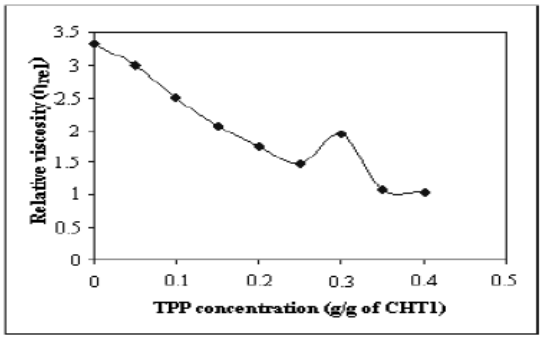


Figure-5
Relative viscosity CHT1 nano solution as a function of TPP concentration

Viscosity behaviour of nano chitosan: The viscosity of polymer solution, at the molecular level, is a direct measure of the hydrodynamic volume of the polymer molecules which in turn is governed by the molecular size or the chain length and hence the molecular weight[25]. Relative viscosity as a function of particle size and the extent to which a parent chitosan scales down to nano level at a given concentration of CHT and TPP are presented graphically in figure 6 and figure 7 respectively.

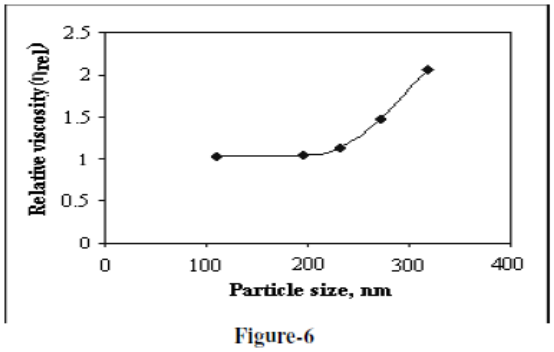


Figure-6
Viscosity as a function of particle size of CHTN

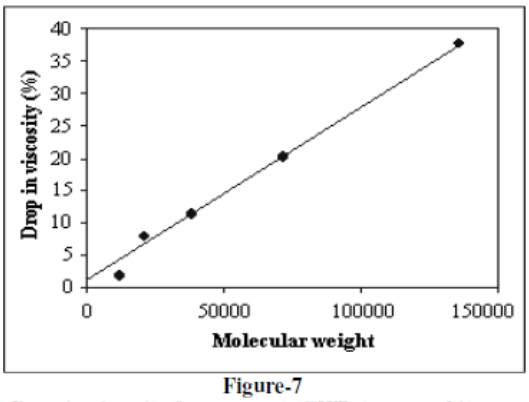


Figure-7
Drop in viscosity from parent (CHT) to nano chitosan (CHTN) solution as a function of molecular weight

It was revealed from figure 6 that the viscosity of CHTN dispersion decreased with reduction in particle size. However, the effect was more significant for larger particles than the smaller one. Obviously, the larger the particle size the higher will be the resistance offered for the flow of liquid and hence the higher will be the viscosity and vise versa. Comparatively slower fall in viscosity for small CHTN particles may be attributed to the low molecular weights of parent chitosan. It is demonstrated in figure 7 that the percentage drop in viscosity from molecular (CHT) solution to corresponding nano chitosan (CHTN) dispersion follows a straight line. It means higher molecular weight chitosan scales down to nano size to greater extent than the lower molecular weight chitosan. This can be explained as follows; large size chitosan molecules in solution accommodate comparatively more amount of solvent and occupy large 'hydrodynamic' volume. These swollen molecules compress to greater extent by ionotropic intramolecular cross linking with TPP by displacing the solvent, as demonstrated in figure 1. On the other hand, the extent of swelling of low molecular weight chitosan is comparatively less[24] and hence lesser will be its tendency to compress.

Stability of nano chitosan dispersion: The biodegradability of chitosan is anticipated to be influenced by its particle size. Therefore the stability behaviour of standing baths of nano chitosan dispersion should be taken into consideration during its applications particularly to textile fabrics. The stability of nano chitosan dispersions for 24 hrs were analysed by viscosity measurements as shown in table 3. The data illustrate that the stability in terms of change in viscosity of parent chitosan (CHT) solution is governed by its molecular weight, which is improved with decrease in molecular weight. The stability behaviour of nano chitosan (CHTN) dispersion, on the other hand, was found to be different from that of parent chitosan solutions. Nano chitosan dispersions obtained from higher molecular weight chitosans are found tobe more stable than the corresponding parent chitosan solutions. Where as the nano

dispersions obtained from low molecular weight chitosans are seen tobe more susceptible to degradation. Complete biodegradation of nano chitosan dispersion, in general, was resulted in 3-4 days showing the formation of white globules as shown in figure 8. Therefore, utilization of nano chitosan dispersions in textile applications within the 24 hrs is advisable. Viscosity analysis and visual observations may be the useful tools for stability inspections.

Table-3
Stability of nano chitosan solution as a function of particle size

Parent chitosan(CHT) solution (1gpl)			Nano chitosan solution(CHTN) (1gpl)		
Sample Code	Molecular Weight, Mv	Change in viscosity (%) after 24 hrs	Sample Code	Particle size (nm)	Change in viscosity (%) after 24 hrs
CHT1	135,839	-10.27	CHT1N	319.4	-3.68
CHT2	71,676	-4.1	CHT2N	271.6	-1.05
CHT3	38,733	-2.6	CHT3N	231.01	-1.18
CHT4	20,698	-2.15	CHT4N	195.2	-3.6
CHT5	11,986	-1.73	CHT5N	110.74	-2.27

Figure-8
Stability study: white globular residue formed by microbial attack on CHT1N

Conclusion

Ionotropic gelation method for the preparation of nano chitosan dispersion using TPP is faster, convenient and non toxic. The concentration of chitosan in the formulation bath has the influence on the particle size. Particle size reduces with decrease in concentration. Direct preparation method gives much reduced size than that of dilution method. With decrease in intrinsic viscosity and hence the molecular weight, the particle size also decreases progressively and shows a curvilinear dependence on particle size. This relation may be useful in preparation nano chitosan dispersion of desired size. TPP concentration determines the particle size. With increase in concentration of TPP, the particle size reduces, reaches to minimum and again increase. Excessive TPP in system leads to precipitation. By reducing the particle size to nano level, the viscosity of chitosan solution is lowered significantly, but the storage stability was affected adversely. Use of freshly prepared nano-chitosan dispersions prior to applications may be the remedy.

References

1. Muzzarelli R.A.A., 'Chitin Chemistry' in: J.C. Salamone, (ed), *The polymeric materials Encyclopedia*, Pub.CRC press Inc.,Boca Raton Fl, USA, 312-314 (**1996**)
2. Hirano S., 'Chitin and Chitosan', *Ullmann's Encyclopedia of Industrial Chemistry*, Pub.Wiely-VCH, **6**, 679-691(**2003**)
3. Oktem T., Surface treatment of cotton fabrics with chitosan, *Col.Tech.* **119**, 241-246 (**2003**).
4. Harish Prashant K.V. and Tharanathan R.N., Chitin/Chitosan: modifications and their unlimited application potential- an overview, *Trends in food Sci. and Tech.* **18**, 117-131, doi:10.1016/j.tifs.2006.10.022 (**2007**)
5. Giri Dev V.R., Neelkandan R., Sudha N., Shamugasundaram O.L. and Nadaraj R.N., Chitosan- A polymer with wider applications, *Text.Magazine,* (**7**), 83-86 (**2005**)
6. Kean T, Roth S, Thanou M, Trimethylated chitosans as non-viral gene delivery vectors: cytotoxicity and transfection efficiency, *J Control Release*, **103** (**3**), 643–53 (**2005**)
7. Daniela Enescu, Use of Chitosan in Surface Modification of Textile Materials, *Roumanian Biotechnological Letters,* **13**(**6**), 4037-4048 (**2008**)
8. Inamdar M.S. and Chattopadhyay D.P., Chitosan And Its Versatile Applications In Textile Processing, *Man Made Text. In India,* **XLIX** (**6**), 212-216 (**2006**)
9. H.K. No, and S.P. Meyers, *J. Aquatic Food Product Tech.*, **4**, 27-52 (**1995**)
10. Chattopadhyay D.P. and Inamdar M.S., Studies on the properties of chitosan treated cotton fabric, *Asian Dye.*, **5** (**6**), 47-53 (**2009**)
11. Seaong Ha-Soo, Kim Jae-Pil and Ko Sohk-Won, Preparing Chito-Oligosaccharide as Antimicrobial Agents for cotton, *Text. Res. J.*, **69**(**7**), 483-488, doi:10.1177/004051759906900704 (**1999**)
12. Gupta Deepti and Saini Komal, Low molecular weight chitosan derivatives for antimicrobial treatment of cotton, *Colourage*, **LV** (**4**), 42- 48 (**2008**)

13. Agnihotri Sunil A. and Mallikarjuna Nadagouda N., Aminabhavi Tejraj M., Recent advances on chitosan-based micro- and nanoparticles in drug delivery, *J. Contr. Rel.*, **100(8)**, 5 –28 **(2004)**, doi:10.1016/j.jconrel.2004.08.010

14. Patel J. K. and Jivani N. P., Chitosan Based Nanoparticles in Drug Delivery, *Int. J.Pharm. Sci. and Nanotech.*, **2(2)**, 517-522 **(2009)**

15. Zhang Hong-liang, Wu Si-hui, Tao Yi, Zang Lin-quan and Su Zheng-quan, Preparation and Characterization of Water-Soluble Chitosan Nanoparticles as Protein Delivery System, *J. Nanomat.*, **2010**, 1-5, doi:10.1155/2010/898910 **(2010)**

16. Trapani Adriana, Sitterberg Johannes, Bakowsky Udo and Kissel Thomas, The potential of glycol chitosan nanoparticles as carrier for low water soluble drugs, *Int. J. Pharm.,* **375,** 97–106, doi:10.1016/j.ijpharm.2009.03.041 **(2009)**

17. Tamura Ayumi, Satoh Erika, Kashiwada Ayumi, Matsuda Kiyomi and Yamada Kazunori, Removal of Alkylphenols by the Combined Use of Tyrosinase Immobilized on Ion-Exchange Resins and Chitosan Beads, *J. Appl. Poly. Sci.*, **115**, 137–145, DOI 10.1002/app.30947 **(2010)**

18. Ge Huacai and Huang Shiying, Microwave Preparation and Adsorption Properties of EDTA-Modified Cross-Linked Chitosan, *J. Appl. Poly. Sci.*, **115**, 514–519, doi 10.1002/app.30843 **(2010)**

19. Lee Hyun Woo, Karim Mohammad Rezaul, Park Jae Hyeung, Ghim Han Do, Choi Jin Hyun, Kim Ketack, Deng Yulin and Yeum Jeong Hyun, Poly(vinyl alcohol)/Chitosan Oligosaccharide Blend Submicrometer Fibers Prepared from Aqueous Solutions by the Electrospinning Method, *J. Appl. Poly. Sci.*, **111**, 132–140 **(2009)**

20. Du Wen-Li, Niu Shan-Shan, Xu Ying-Lei, Xu Zi-Rong and Fan Cheng-Li, Antibacterial activity of chitosan tripolyphosphate nanoparticles loaded with various metal ions, *Carb. Polym.*, **75,** 385–389, doi:10.1016/j.carbpol.2008.07.039 **(2009)**

21. Chattopadhyay D.P. and Inamdar M.S., Aqueous Behaviour of Chitosan, *Int. J. Poly. Sci.*, 2010, 1-7, doi:10.1155/2010/939536 **(2010)**

22. Knaul Jonathan Z., Kassai Mohammad R., Bui V. Tam and Greber Katherine A.M., Characterization of deacetylated chitosan and chitosan molecular weight –review, *Can J. Chem.*, **76(11)**, 1699- 1706 **(1998)**

23. Gowariker V.R., Viswanathan N.V. and Sreedhar Y., Polymer Solutions, *Polymer Science,* Pub. New Age International Publisher, N.Dehli, India, 332-362 **(1986)**

24. Tager A., Rheological properties of polymers in viscofluid state, *Physical Chemistry of Polymers,* MIR Publishers-Moscow, 241-272 **(1972)**

25. Shaw Dunkan J., Rheology, *Introduction to Colloid and Surface Chemistry,* Fourth Edition, Butterworth-Heinemann, Oxford (UK) 244-260 **(1992)**

26. Lopez-Leon T., Carvalho E.L.S., Seijo B., Ortega-Vinuesa J.L. and Bastos-Gonzalez D., Physicochemical characterization of chitosan nanoparticles: electrokinetic and stability behavior, *J. Coll. Interface Sci.*, **283**, 344–351 **(2005)**

27. Wang Rong-Min, He Nai-Pu, Song Peng-Fei, He Yu-Feng, Ding Lan and Lei Zi-Qiang, Preparation of nano-chitosan Schiff-base copper complexes and their anticancer activity, *Polym. Adv. Technol.*, **20**, 959–964 **(2009)**

28. Wang Tao and Gunasekaran Sundaram, State of Water in Chitosan–PVA Hydrogel, *J. Appl. Poly. Sci.*, **101**, 3227–3232 **(2006)**

29. Boonyo Worawan, Junginger Hans E., Waranuch Neti, Polnok Assadang and Pitaksuteepong Tasana, Preparation and Characterization of Particles from Chitosan with Different Molecular Weights and Their Trimethyl Chitosan Derivatives for Nasal Immunization, *J. Met. Mat. Min.,* **18(2)**, 59-65 **(2008)**

30. Loretz B. and Bernkop–Schnürch A., In vitro evaluation of chitosan–EDTA conjugates polyplexes as a nanoparticulate gene delivery system, *AAPS J,* **8**(4), 85 **(2006)**

31. Huang Kuo-Shien, Sheu Yea-Ru and Chao In-Chun, Preparation and properties of nanochitosan, *Poly.Plast. Tech.Eng.*, **48**, 1239- 1243 **(2009)**

32. Gong Jingming, Hu Xianluo, Wong Ka-wai, Zheng Zhi, Yang Lin, Lau Woon-ming and Du Ruxu, Chitosan Nanostructures with Controllable Morphology Produced by a Nonaqueous Electrochemical Approach, *Adv. Mater.,* **20** 2111–2115 **(2008)**

33. Hebeish A., Waly A. and Aou-Okeil A., The effect of molecular weight of chitosan on cotton fabric treated with citric acid and its impact on dyeing with some acid dyes, *J. Text. A.,* **65(5)**, 219-227 **(2005)**

Hindawi Publishing Corporation
International Journal of Polymer Science
Volume 2010, Article ID 939536, 7 pages
doi:10.1155/2010/939536

Research Article

Aqueous Behaviour of Chitosan

D. P. Chattopadhyay[1] and Milind S. Inamdar[2]

[1] *Department of Textile Chemistry, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara 390001, India*
[2] *Faculty of Textile Processing, Sarvajanik College of Engineering and Technology, Surat 395001, India*

Correspondence should be addressed to D. P. Chattopadhyay, dpchat6@gmail.com

Received 27 September 2010; Revised 6 December 2010; Accepted 30 December 2010

Academic Editor: Peter J. Halley

Chitosan, a versatile biopolymer, finds numerous applications in textile processing unit operations such as preparation, dyeing, printing, and finishing. However, the accessibility of this biopolymer by the textile material depends on the viscosity of its solution which in turn is a function of its molecular weight. In this work, therefore, the effect of molecular weight, storage life, presence of electrolyte, and particle size of chitosan on its viscosity was investigated. Chitosan of different molecular weights was synthesized by nitrous acid hydrolysis of parent chitosan solution. The synthesized low molecular weight products were analysed by FTIR spectroscopy. Chitosan of nanoconfiguration was prepared by Ionotropic gelation method and characterized by particle size analyzer. The viscosity of different chitosan solutions was determined using Ubbelohde capillary viscometer. As an extension to this study, the chelation property of chitosan was also evaluated.

1. Introduction

Chitosan, a versatile biopolymer derivative, is obtained by alkaline deacetylation of chitin. The distribution of the precursor, chitin, in nature is ubiquitous among the shells of crustaceans such as crabs, shrimps, and lobsters as well as in the exoskeleton of marine zoo-plankton including coral, jellyfish, and squid pens. Chemically, chitosan is a linear (1-4) linked 2-amino-2-deoxy-β-d-glucan (i.e., β-d-glucosamine) in the chair $^4C_1$ conformation, Figure 1. The structure of chitosan closely resembles that of cellulose, except an hydroxyl group at C2 position in cellulose being replaced by amino group in chitosan. Indeed, it is a copolymer of glucosamine and N-acetyl glucosamine units. Chitosan exhibits several valuable inherent properties such as antibacterial, antifungal, antiviral, antacid, nontoxic, total biodegradable as well as film formation, fibre formation, and hydrogel formation properties [1, 2]. By virtue of these properties, chitosan has prospective applications in many fields such as medical, waste water treatment, cosmetics, dentifrices, food, agriculture, pulp and paper, and textile industries [3, 4].

In textiles, it finds applications in the primary production of fibres (useful for sutures, wound dressings, etc.), in the manufacture of textile auxiliary chemicals and finishing agents [5–7]. Investigations have shown that it can improve the dye uptake of cotton fibre [8]. It can also be used as a dye-fixing agent, for shade and naps coverage, to improve the fastness of dyed fabrics, as a binder in pigment printing, as a thickener in printing [9]. It is also found that the treatment of wool with chitosan minimizes its felting problem. The bioadhesive and cationic nature of chitosan enables it to form a strongly adhered film on individual fibres and prevent their entanglements [10]. By virtue of its antibacterial property, chitosan can prevent garments to develop bad odour [11–13].

Chitosan when dissolved in acidic solution gives viscous solutions. The viscosity determines the extent of penetration of chitosan into the fabric structure. In solutions, chitosan in suitable conditions shows hydrogel formation and viscoelastic behaviour [14–17]. Its rheological behaviour to characterize its usefulness as thickener in printing paste is reported [18]. However its aqueous behaviour pertaining to various unit operations of textile processing is hardly

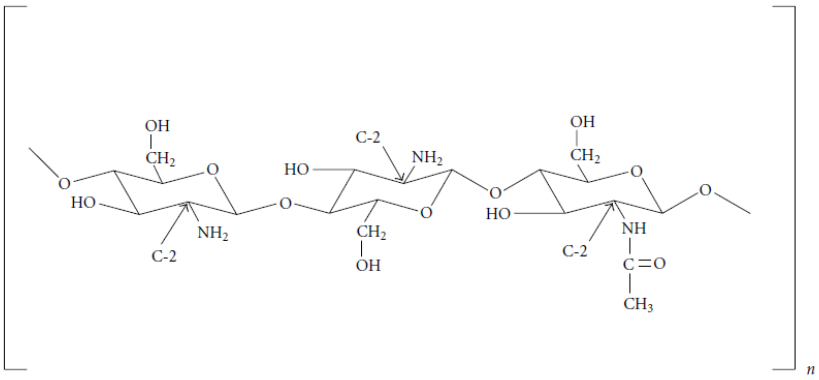


Figure 1: Structure of chitosan.

Table 1: Specifications of different chitosans.

Particulars	Specifications	
Nomenclature	CHT1	CHT3
DAC Value (%)	89.03	90
Viscosity (m Pa·s)	183	22
Molecular Weight	654, 127	135, 839

reported in the literature. The present research work, therefore, mainly aimed at investigating the aqueous behaviour of chitosan with respect to its molecular weight, concentration and particle size on viscosity and stability of its solution. The effect of electrolytes such as sodium acetate is also reported. The work is also extended to study the chelation behaviour of chitosan.

2. Materials and Methods

2.1. Materials. Chitosan samples of different molecular weights were purchased from M/s Marine chemicals, Kerala state, India (CHT1) and M/s Mahtani Chitosan Pvt. Ltd., Gujarat State, India (CHT3). The molecular weights of these samples were determined viscometrically. The specifications of different chitosans are given in Table 1.

Other chemicals such as acetic acid, sodium acetate, sodium hydroxide, trisodium polyphosphate (TPP), methanol, and tetra sodium salt of ethylene diamine tetra acetic acid (Na_4EDTA) and used were of analytical grade of reputed companies.

2.2. Synthesis of Low Molecular Weight Chitosan. Low molecular weight chitosans were synthesized by controlled hydrolysis of chitosan using nitrous acid as depolymerising agent. A 2% solution of chitosan in acetic acid was prepared. Predissolved dilute solution of sodium nitrite was then added gradually to chitosan solution and stirred for two hrs at 30°C to get desired viscosity level. The depolymerized chitosan was then precipitated out by caustic solution and washed to neutral pH. The precipitates of chitosan was then washed 3 to 4 times with methanol and dried at 60°C. The product obtained from CHT1 is termed as CHT2 whereas the products obtained from CHT3 are termed as CHT4 & CHT5.

2.3. Determination of Molecular Weight and Viscosity. The molecular weight and viscosity behaviour of chitosan was determined using Ubbelohde capillary viscometer (No 1A) at 30°C having flow time for distilled water, T_0 = 15.57 seconds. Chitosan solutions of different concentrations in 0.25 M acetic acid and 0.25 M sodium acetate were prepared. During preparation, all the solutions were magnetically stirred for 1 hour to ensure proper dissolution of chitosan and were filtered using Whatman filter paper no 4. The flow times of chitosan solutions and solvent were recorded in triplicate and the average value was calculated. The intrinsic viscosity $[\eta]$ was calculated graphically by extrapolating the curve of reduced viscosity versus concentration to zero concentration. The molecular weight was then calculated by using Mark-Houwink equation (1) [19].

2.4. FTIR Analysis. FTIR spectra of chitosan and depolymerised chitosan samples were recorded on a Thermo Nicolet iS10 Smart ITR spectrophotometer (Thermo Fisher Scientific, USA), equipped with an OMNIC-Software, a DTGS detector, and a Ge-on-KBr beamsplitter (4000–500 cm^{-1}).

2.5. Preparation of Nanochitosan and Its Characterization. Chitosan (CHT3) was dissolved in acetic acid solution and optimized quantity of TPP was added dropwise with rapid stirring (about 400 rpm) to obtain an opalescent solution containing chitosan 25 mg/dL and TPP 3.75 mg/dL. The sample was allowed to stand overnight and filtered through sintered glass filter of porosity grade G3 and preserved in refrigerator. The prepared chitosan was coded as CHT3N.

The particle size and size distribution of the chitosan were analyzed on the particle size analyser (Model: Zetasizer Nano-ZS90, Make: Malvern Instruments Ltd, UK).

2.6. Evaluation of Metal Ion Chelation Value in Water. The amount of Ca^{+2} as calcium chloride in water for chelation study were determined by volumetric analysis of 50 mL sample against 0.02 M Na_2EDTA solution using Eriochrome black T indicator.

3. Results and Discussion

3.1. Effect of Molecular Weight and Concentration. Chitosan is characterized mainly by two variables, namely, degree of deacetylation (DAC value) and the molecular weight. Degree of deacetylation determines the number of free amino groups present in the chitosan macromolecule, which in turn determines the functionality, polarity, and water solubility of the polymer. On the other hand, molecular weight determines the strength of its fiber/film and viscosity of its solution. Different molecular weight chitosan can be obtained by controlled depolymerization by methods such as acid hydrolysis (HCl, HNO_2, etc.), free radicals (H_2O_2, $K_2S_2O_8$), enzymatic, radiations (UV, γ rays) ultrasound, microwave, and thermal treatments [3, 20–24].

When chitosan solution is treated with nitrous acid, produced from acidic solution of sodium nitrite, it undergoes deamination reaction with subsequent cleavage of β-glycosidic linkages. The reaction scheme and FTIR spectra are illustrated in Figures 2 and 3, respectively.

It envisaged from Figure 3 that the IR spectra of chitosan and depolymerised chitosan are almost similar which indicates that the process of depolymerisation caused no chemical change in the structure of the polymer except reduction in molecular weight which is evident from the change in viscosity.

The viscosity of polymer solution, at the molecular level, is a direct measure of the hydrodynamic volume of the polymer molecules which in turn is governed by the molecular size or the chain length and hence the molecular weight [25]. Therefore, viscosity, measured by capillary viscometer, is widely employed to determine the average molecular weight of a polymer by using the famous Mark-Houwink equation (1)

$$[\eta] = k[M_V]^{\alpha}, \tag{1}$$

where M_V is the viscosity average molecular weight of polymer, α and k are constants ($\alpha = 0.83$ and $k = 1.4 \times 10^{-4}$ for 0.25 M acetic acid and 0.25 M sodium acetate solvent system) [26], and $[\eta]$ is the limiting viscosity number or intrinsic viscosity and can be determined from [19]

$$[\eta] = \lim_{C \to 0} \frac{(\eta - \eta_s)}{\eta_s C}, \tag{2}$$

where η is the solution viscosity and η_s is the solvent viscosity and C is the solution concentration. As indicated in (2), when $(\eta - \eta_s)/\eta_s C$, that is, reduced viscosity (η_{red}) is plotted against concentration (C), the intercept corresponds to intrinsic viscosity $[\eta]$. Such plots for different grades of chitosan are shown in Figure 4 and the corresponding intrinsic viscosities and calculated molecular weights are presented in Table 2.

Table 2: Intrinsic viscosity and viscosity average molecular weight of different grades of chitosan.

Chitosan	Intrinsic viscosity $[\eta]$, dL/g	Molecular weight, M_V
CHT-1	9.40	654, 127
CHT-2	4.72	285, 231
CHT-3	2.55	135, 839
CHT-4	1.50	71, 676
CHT-5	0.535	20, 698

It can be seen from Figure 4 that the curves of high molecular weight chitosan, namely, CHT-1, 2, and 3, do not strictly follow the linearity of (2). They show the inflection at a certain critical concentration (C^*) and then after the curves bend upwards. Further, the value of C^* increases with decrease in molecular weight and ultimately the curves flatten for lower molecular weight chitosans. This can be explained as follows: when chitosan or any other polymer is added into a solvent, the solvent gradually diffuse into the polymer aggregates resulting into the swelling of the polymer. As swelling continues, the segments of the polymer are solvated and loosened out. Since the molecules in a solid polymer remains entangled with neighbouring ones, polymer molecules during dissolution diffuse out as bunches of entangled molecules. Even when all chain segments of a polymer molecule in solution are unfolded and fully solvated, the molecules do not assume the shape of an extended straight chain but present in a coil form. These coils or aggregates offer resistance for the mobility or flow of molecules and hence impart viscosity [19, 27]. When the molecular size and concentration is increased, as in our case, the extent of entanglement is increased. In other word, the critical concentration (C^*) is, indeed, the "overlap" concentration. When $C > C^*$ the intermolecular entanglements or aggregation, predominate and preclude the overall molecular motion of the polymer, while individual polymer molecules are statistically separated from other molecules at $C < C^*$. Thus, the critical concentration (C^*) is a measure of molecular size and conformation of a polymer. The higher the molecular weight and the more rigid is the conformation, the lower the value of C^*. The results are in close agreement with the earlier reports [15, 28].

3.2. Effect of Storage Time on Viscosity of Chitosan Solution. Polymeric chemicals are generally applied to textiles by padding technique where it is required to prepare a standing bath. Thus the chemical remains in contact with water for a longer period. As biodegradability of chitosan is a well-known phenomenon the effect of storage time on the stability of its solution was studied in terms of change in solution viscosity. It is seen from Figure 5 that the viscosity of chitosan solution is adversely affected with increase in storage time.

It seems that the initial molecular weight and the concentration of polymer has the influence on the stability

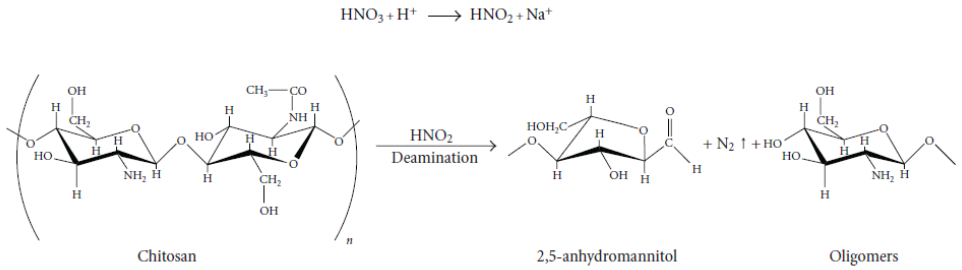


Figure 2: Depolymerization of chitosan by nitrous acid.

Table 3: Chelation property of chitosan.

Treatment	Concentration, gpl	Amount of Ca^{+2} ions (ppm) chelated after:				
		2 hrs	24 hrs	48 hrs	72 hrs	96 hrs
Na_4EDTA	1	405	426	435	450	452
CHT1	1	177	208	232	269	293
CHT3	1	182	187	185	189	196

Initial concentration of Ca^{+2} in water = 625 ppm.

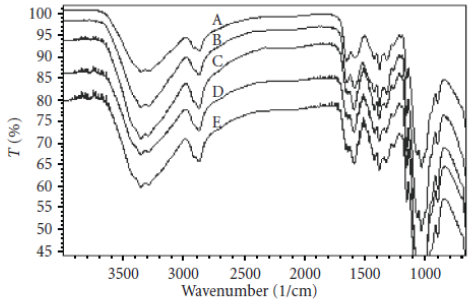


Figure 3: FTIR spectra of CHT1 (A), CHT2 (B), CHT3(C), CHT4 (D) and CHT5 (E).

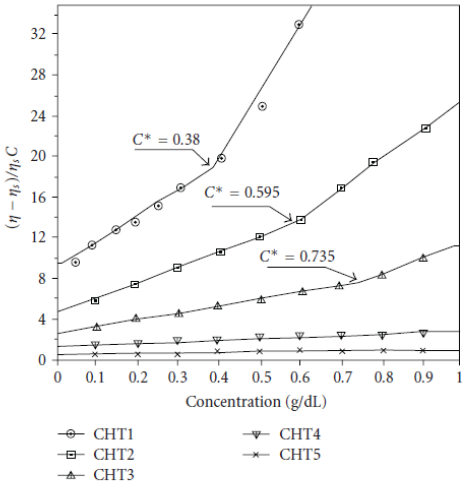


Figure 4: Intrinsic viscosities of different grades of chitosan.

of the solution. Initially the curve shows segments with an overlap concentration (C^*) at the point of inflection and then flattens as the storage time is increased, that is, the critical concentration shifts towards right. It is also observed that the drop in viscosity in first 24 hrs is much faster than the latter and is more significant at higher concentration, that is, above C^*. The loss in viscosity may be attributed to the biodegradation of chitosan molecules and/or hydrolysis of polymer molecules. Initially the large molecules, especially at higher concentration, occupy large "hydrodynamic" volume, which leads to less mobility indicating higher viscosity. The hydrolytic degradation of the polymer leads to the production of smaller molecular entities which in turn causes a drop in hydrodynamic volume of the polymer molecules resulting in higher molecular mobility and as a result reduces the viscosity of the solution [19, 27, 28].

3.3. Effect of Electrolyte on Viscosity of Chitosan. Chitosan is known to be a polycationic material; its solution is believed to be influenced by the presence of electrolytes. Therefore, the effect of sodium acetate concentrations on two different grades of chitosan namely, CHT 1 and CHT 3 was studied.

It can be seen from Figure 6 that the viscosity is sharply reduced in presence of sodium acetate up to a concentration of about 2 g/dL. Further increase in concentration has not influenced the viscosity much. It is also observed that the

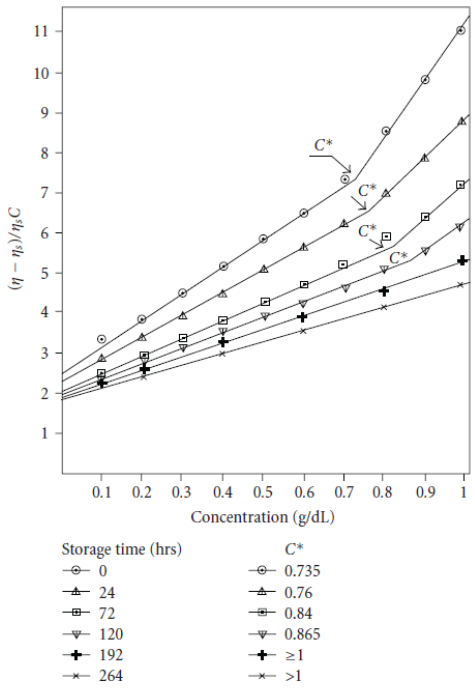


Figure 5: Viscosity of chitosan (CHT-3) solution as a function of storage time.

chitosan with higher molecular weight (CHT1) is more affected compared with its lower molecular counterpart (CHT2). The decrease in viscosity with increase in electrolyte concentration can be attributed to the shielding effect of counter ions [29]. Due to ion dipole forces, the acetate ions form a cascade of negative charge over each chitosan molecules establishing repulsive forces between them. This offers low resistance to the flow or mobility of the polymer molecules.

3.4. Effect of Particle Size on Viscosity of Chitosan. It is possible, for a given molecular size chitosan, to scale down the hydrodynamic volume to nanolevel by means of ionotropic gelation using suitable cross linking agent such as sodium tripolyphosphate (TPP), as illustrated in Figure 7. The particles are stabilized by electrostatic hindrance due to coulombic repulsion between particles of same ionic charges [30–32]. We prepared nanochitosan (CHT3N) of average size 394.8 nm from 0.25 gpl CHT3. The particle size distribution and viscosity behaviour of this nanosolution are show in Figures 8 and 9, respectively.

The particle size of chitosan is found to affect its viscosity behaviour significantly (Figure 9). The viscosity of nanochitosan colloid is dropped by about 30% with respect to normal chitosan solution at the same concentration level.

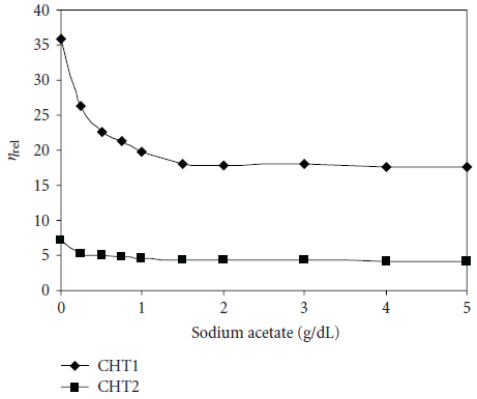


Figure 6: Relative viscosity of chitosan solution as a function of electrolyte concentration.

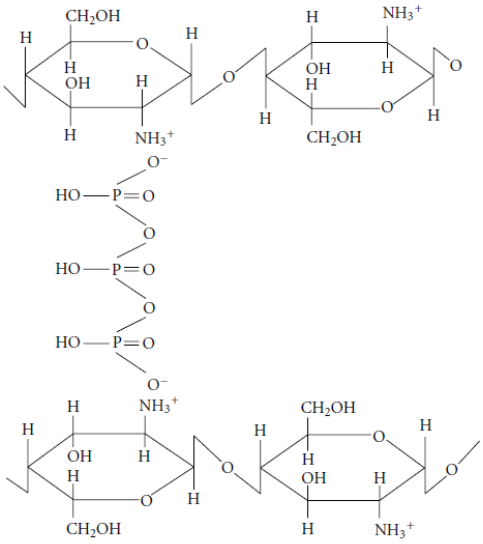


Figure 7: Ionotropic cross-linking of chitosan and TPP.

The reduction of size to nanolevel has also influenced the stability of chitosan solution. There is 10% drop in the viscosity of normal chitosan for a storage time of 24 hours, whereas nano colloids dropped by 17% for the same storage time. Thus reduction in size reduced the storage stability of the polymer. The reduction in viscosity of nano chitosan solution can be attributed to its lesser resistance towards flow due to its smaller size and enhanced degradation of the polymer in solution due to higher exposed surface area of the nanoparticles.

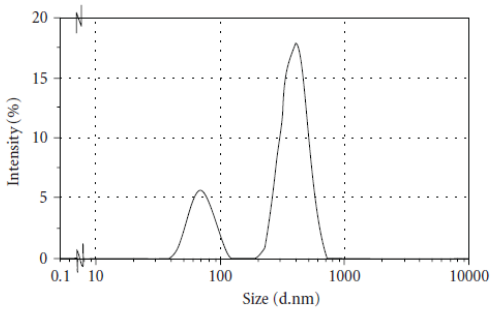


Figure 8: Size distribution of nanochitosan (CHT3N).

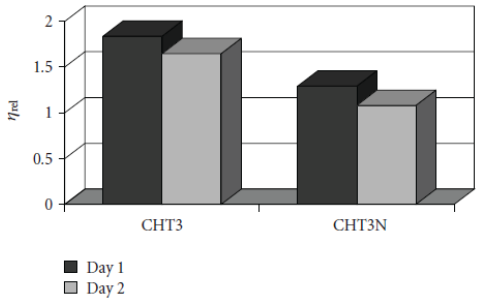


Figure 9: Relative viscosity of chitosan solution as a function of particle size.

3.5. Chelation Property of Chitosan. Attributing to the presence of large number of amino groups on chitosan backbone, this biopolymer can also be used in water processing engineering. Chitosan molecules are known to chelate anionic dyes in waste dye solution and flocculate them out.

It has also been found that the chitosan and its derivatives can remove phosphorus, heavy metals, and oils from water [33–37]. In order to study the chelation property of chitosan, the removal of calcium ions from water by CHT1 and CHT3 was determined and the results were compared with Na_4EDTA. Table 3 shows that chitosan can remove the calcium ions substantially though its sequestering power is found to be inferior to EDTA. Further, it is observed that maximum removal occurred in the first 2 hours. Higher molecular weight sample, CHT1 shows better chelation power compared with its lower molecular weight counterpart, CHT3. The former one also shows a continuation in chelation effect even after 96 hrs without reaching the equilibrium, whereas the rest of the samples reached equilibrium within 24 hrs. A substantial higher chelation of Na_4EDTA may be attributed to the combined effect of both carboxylate and amino groups present in its molecule and possibly higher proximity of each molecule due to its relatively small size. The larger molecular size of chitosan provides less surface area and the less amino groups to form the coordinate linkage with calcium ions. The prolonged chelation effect of CHT1 is found probably due to gradual disentanglement of the polymer molecules with respect to time.

4. Conclusions

The viscosity of chitosan is influenced by its molecular weight. Curves of reduced viscosity verses concentration for higher molecular weight chitosan show inflection point, that is, a critical or overlap concentration (C^*). The overlap concentration (C^*) is a measure of molecular size and conformation of a polymer.

The higher the molecular weight and the more rigid is the conformation and lower is the value of C^*. The initial molecular weight and the concentration of chitosan are found to influence the stability of its solution. The drop in viscosity in first 24 hrs is found to be very fast, and the critical/overlap concentration (C^*) point shifts towards right when the storage time is prolonged.

In presence of electrolyte, the viscosity of chitosan solution is reduced, which is found to be more pronounced for high molecular weight chitosan solution.

By reducing the particle size to nanolevel, the viscosity of chitosan solution is lowered significantly, but the storage stability was affected adversely. Use of freshly prepared nanochitosan solution prior to applications may be the remedy.

Chitosan exhibits chelation property. This property is useful in removing metal and dye ions from water.

References

[1] S. Hirano, *ULLMANN's Encyclopedia of Industrial Chemistry*, vol. 7, Wiley-VCH, Weinheim, Germany, 6th edition, 2003.

[2] R. A. A. Muzzarelli, "Chitin chemistry," in *The Polymeric Materials Encyclopedia*, J. C. Salamone, Ed., pp. 312–314, CRC Press, Boca Raton Fla, USA, 1996.

[3] K. V. Harish Prashanth and R. N. Tharanathan, "Chitin/chitosan: modifications and their unlimited application potential-an overview," *Trends in Food Science and Technology*, vol. 18, no. 3, pp. 117–131, 2007.

[4] P. K. Dutta, J. Duta, and V. S. Tripathi, "Chitin and Chitosan: chemistry, properties and applications," *Journal of Scientific & Industrial Research*, vol. 63, no. 1, pp. 20–31, 2004.

[5] Y.-S. Chung, K.-K. Lee, and J.-W. Kim, "Durable press and antimicrobial finishing of cotton fabrics with a citric acid and chitosan treatment," *Textile Research Journal*, vol. 68, no. 10, pp. 772–775, 1998.

[6] W. B. Achwal, "Chitosan and its derivatives for textile finishing," *Colourage*, vol. 50, no. 8, pp. 51–76, 2003.

[7] A. J. Rigby, S. C. Anand, and A. R. Horrocks, "Textile materials for medical and healthcare applications," *Journal of the Textile Institute*, vol. 88, no. 1, pp. 83–93, 1997.

[8] D. P. Chattopadhyay and M. S. Inamdar, "Studies on the properties of chitosan treated cotton fabric," *Asian Dyer*, vol. 6, no. 5, pp. 47–53, 2009.

[9] S. A. Bahmani, G. C. East, and I. Holme, "The application of chitosan in pigment printing," *Journal of the Society of Dyers and Colourists*, vol. 116, no. 3, pp. 94–99, 2000.

[10] P. Erra, R. Molina, D. Jocic, M. R. Julia, A. Cuesta, and J. M. D. Tascon, "Shrinkage properties of wool treated with

low temperature plasma and chitosan biopolymer," *Textile Research Journal*, vol. 69, no. 11, pp. 811–815, 1999.

[11] D. Knittel and E. Schollmeyer, "Chitosan and its derivatives for textile finishing," *Melliand Textilberichte*, vol. 83, no. 1-2, pp. E15–E16, 2002.

[12] Z. Zhang, L. Chen, J. Ji, Y. Huang, and D. Chen, "Antibacterial properties of cotton fabrics treated with Chitosan," *Textile Research Journal*, vol. 73, no. 12, pp. 1103–1106, 2003.

[13] I. Holme, "Antimicrobials impart durable freshness," *International Dyer*, vol. 187, no. 12, pp. 9–11, 2002.

[14] M. A. Torres, A. M. Beppu, C. C. Santana, and E. J. Arruda, "Viscoelastic properties of chitosan solutions and gels," *Brazilian Journal of Food Technology*, vol. 9, no. 2, pp. 101–108, 2006.

[15] R. Shepherd, S. Reader, and A. Falshaw, "Chitosan functional properties," *Glycoconjugate Journal*, vol. 14, no. 4, pp. 535–542, 1997.

[16] C. L. Velásquez, J. S. Albornoz, and E. M. Barrios, "Viscometric stidies of chitosan nitrate and chitosan chlorhydrate in acid free NaCl aq solution," *e-Polymers*, no.014, 2008.

[17] M. Sano, O. Hosoya, S. Taoka et al., "Relationship between solubility of chitosan in alcoholic solution and its gelation," *Chemical and Pharmaceutical Bulletin*, vol. 47, no. 7, pp. 1044–1046, 1999.

[18] S. K. Tiwari and M. M. Gharia, "Characterization of chitosan pastes and their application in textile printing," *AATCC Review*, vol. 3, no. 4, pp. 17–19, 2003.

[19] V. R. Gowariker, N. V. Viswanathan, and Y. Sreedhar, "Polymer solutions," in *Polymer Science*, pp. 332–362, New Age International, New Delhi, India, 1986.

[20] A. Hebeish, A. Waly, and A. Aou-Okeil, "The effect of molecular weight of chitosan on cotton fabric treated with citric acid and its impact on dyeing with some acid dyes," *Journal of the Textile Association*, vol. 65, no. 5, pp. 219–227, 2005.

[21] H. S. Seong, J. P. Kim, and S. W. Ko, "Preparing chitooligosaccharides as antimicrobial agents for cotton," *Textile Research Journal*, vol. 69, no. 7, pp. 483–488, 1999.

[22] F. Lee, W. K. Lee, M. Y. Maskat et al., "Partial depolymerization of chitosan with the aid of bromelain," *Pakistan Journal of Biological Sciences*, vol. 8, no. 1, pp. 73–77, 2005.

[23] F. Tian, Y. Liu, K. Hu, and B. Zhao, "The depolymerization mechanism of chitosan by hydrogen peroxide," *Journal of Materials Science*, vol. 38, no. 23, pp. 4709–4712, 2003.

[24] S. Trzciński, "Combined degradation of chitosans," *Polish Chitin Society, Monograph*, vol. 11, pp. 103–111, 2006.

[25] D. J. Shaw, "Rheology," in *Introduction to Colloid and Surface Chemistry*, pp. 244–260, Butterworth-Heinemann, Oxford, UK, 4th edition, 1992.

[26] J. Z. Knaul, V. T. Bui, K. A. M. Creber, and M. R. Kasaai, "Characterization of deacetylated chitosan and chitosan molecular weight review," *Canadian Journal of Chemistry*, vol. 76, no. 11, pp. 1699–1706, 1998.

[27] A. Tager, "Rheological properties of polymers in viscofluid state," in *Physical Chemistry of Polymers*, pp. 241–272, MIR Publishers, Moscow, Russia, 1972.

[28] J. K. Hwang and H. H. Shin, "Rheological properties of chitosan solutions," *Korea-Australia Rheology Journal*, vol. 12, no. 3-4, pp. 175–179, 2000.

[29] M. Terbojevich and R. A. A. Muzzarelli, "Chitosan," in *Handbook of Hydrocolloids*, G. O. Phillips and P. A. Williams, Eds., pp. 367–378, Woodhead Publishing, Cambridge, UK, 2000.

[30] R. D. Bhumkar and V. B. Pokharkar, "Studies on effect of pH on cross-linking of Chitosan with sodium tripolyphosphate: a technical note," *AAPS PharmSciTech*, vol. 7, no. 2, pp. E1–E6, 2006.

[31] Y. Wu, W. Yang, C. Wang, J. Hu, and S. Fu, "Chitosan nanoparticles as a novel delivery system for ammonium glycyrrhizinate," *International Journal of Pharmaceutics*, vol. 295, no. 1-2, pp. 235–245, 2005.

[32] T. López-León, E. L. S. Carvalho, B. Seijo, J. L. Ortega-Vinuesa, and D. Bastos-González, "Physicochemical characterization of chitosan nanoparticles: electrokinetic and stability behavior," *Journal of Colloid and Interface Science*, vol. 283, no. 2, pp. 344–351, 2005.

[33] S. M. Nomanbhay and K. Palanisamy, "Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal," *Electronic Journal of Biotechnology*, vol. 8, no. 1, pp. 43–53, 2005.

[34] B. Smith, T. Koonce, and S. Hudson, "Decolorizing dye wastewater using chitosan," *American Dyestuff Reporter*, vol. 82, no. 10, pp. 18–66, 1993.

[35] J. A. Laszlo, "Removing acid dyes from textile wastewater using biomass for decolorization," *American Dyestuff Reporter*, vol. 83, no. 8, pp. 17–21, 1994.

[36] P. K. Dutta, K. Durga Bhavani, and N. Sharma, "Adsorption for dyehouse effluent by low cost adsorbent (Chitosan)," *Asian Textile Journal*, vol. 10, no. 1, pp. 57–63, 2001.

[37] H. Ge and S. Huang, "Microwave preparation and adsorption properties of EDTA-modified cross-linked chitosan," *Journal of Applied Polymer Science*, vol. 115, no. 1, pp. 514–519, 2010.

Studies on the properties of chitosan treated cotton fabric

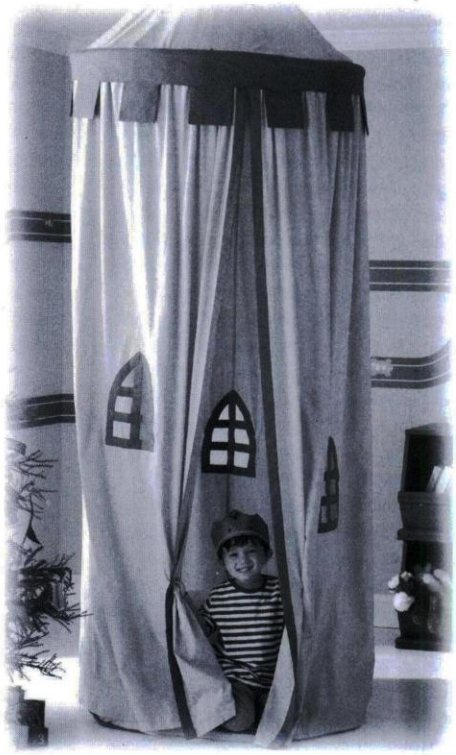
D P Chattopadhyay and M S Inamdar

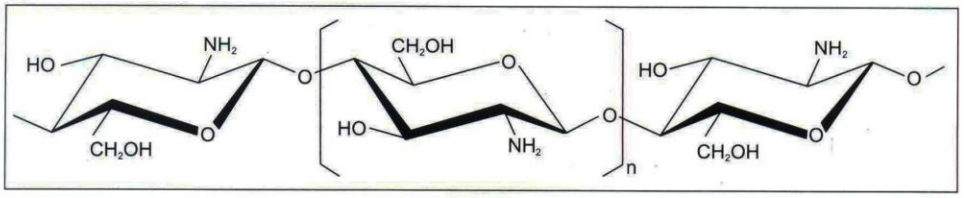
Chitosan is a natural based polymer obtained by alkaline deacetylation of chitin. The precursor, chitin, is widely distributed in shells of crustaceans such as crabs, shrimps, lobsters etc as well as in the exoskeleton of marine zoo-plankton, including coral, jellyfish and squid pens etc with the abundance ranking next to cellulose and is renewable. The structure of chitosan is very much close to that of cellulose except that the hydroxyl group in C(2) position of cellulose is being replaced by amino group in chitosan.It is composed of linear (1-4) linked 2- amino-2-deoxy-β-d-glucan (i.e. β-d-glucosamine) in the chair $^4C_1$ conformation. Indeed, it is a copolymer of N-acetyl-glucosamine and glucosamine units.

Chitosan can be taken as a valuable wet processing agent, but faces several challenges while exploring its applicability.

Chitosan is a white fibrous material produced in different grades according to the degree of deacetylation and molecular weight. Chitosan, being a primary aliphatic amine, can be protonated by various acids. It is insoluble in water, organic solvents and alkalies, but is soluble in organic acid solutions[1,2,3].

Chitosan exhibits several valuable inherent properties such as antibacterial, antifungal, antiviral, antacid, non toxic, total biodegradable as well as film formation, fibre formation, hydrogel formation etc. By virtue of these properties, chitosan has prospective applications in many fields such as biomedical, waste water treatment, cosmetics, dentifrices, food, agriculture, pulp and paper, and textile industries[4,5,6,7,8,9].





Chitosan

In textiles, it finds applications in the primary production of fibres (useful for sutures, wound dressings etc), in the manufacture of textile auxiliary chemicals and finishing agents. Investigations have shown that it can be used as a dye fixing agent, for shade and naps coverage, to improve the fastness of dyed fabrics, as a binder in pigment printing, as a thickener in printing etc. By virtue of its bacteria impeding property, chitosan can prevent garments to develop bad odour [2,5,10,11,12,13,14,15]. Tahlawy[16] studied the effect of chitosan in the finishing of cotton with citric acid in presence of sodium hypophosphite catalyst. He reported a recovery of losses (due to citric acid treatment) in dye uptake and tensile strength, and improved wrinkle recovery by the addition of chitosan in citric acid bath. The whiteness index, however, was deteriorated. In a similar study, Chung et al[17] showed, besides improved wrinkle recovery and D P rating, a high antimicrobial property level which retained through twenty washing and tumble drying cycles. Zhang et al[18] conducted an experiment to study the effect of concentration, molecular weight and degree of deacetylation of chitosan on antibacterial activity to Escherichia coli and Hay bacillus bacteria. They reported a complete inhibition of these bacteria at 0.5 gpl chitosan concentration. They also observed the increased reduction rate of bacteria with increase in molecular weight and degree of deacetylation. Tiwari and Gharia[19] attempted to use chitosan as a thickener in printing paste. Performance of the prints with respect to K/S, wash fastness, crock fastness and hand were observed to be unsatisfactory. Similar attempts were made by Bahmani et al[20] to use chitosan in pigment printing. They showed the prints of satisfactory colour fastness to rubbing, washing and light; however, the major problems were the poor colour value and stiffness of the printed fabric. These suggest that the modification of chitosan is desired. Dutta et al[21] and Abdel-mohdy et al[22] found chitosan to be useful in effluent treatment by virtue of its adsorbing qualities of dyestuffs and various heavy metal ions. In a recent work, modified chitosans' application to cotton made it possible to dye cotton in absence of salt with much higher dye exhaustion compared to the conventional dyeing using recommended quantities of salt[23]. Young Ho Kim et al[24] synthesised quaternary ammonium derivative, N-(2-hydroxy)propyl-3-trimethyl ammonium chitosan chloride by using a reaction of glycidyltrimethylammonium chloride with chitosan. They were able to obtain 100% bacteria reduction at only 0.025% of this derivative as against only 30% bacteria reduction at 1% chitosan. Pourjavadi[25,26] graft copolymerised chitosan with polyacrylamide and methacrylonitrile using ammonium persulphate initiator in order to impart desired properties to chitosan such as superabsorbancy, controlled drug release etc. Grafting can also be carried through hydroxyl groups while protecting the useful amino groups on chitosan backbone. Gorochovceva et al[27] successfully grafted polyethylene glycol at hydroxyl groups through the cynuric chloride bridging.

In this paper, research findings on the effect of applications of chitosan on the dyeing and finishing properties of cotton have been reported. The chitosan was used both as a pre- and post-dyeing agents to investigate its effect on the dyeability and fastness properties of cotton with various direct dyes. The effect of chitosan pre-treatment on the dyeability towards acid dye was also investigated. This biopolymer was used as a finishing agent with an intention to incorporate crease resistant property to cotton. Its effect was compared with the commercially available wrinkle resistant agents and also examined its compatibility with them. The molecular weight of chitosan governs the viscosity of its solution and hence the extent of penetration into the fabric structure. The studies were, therefore, extended to chitosan of varying molecular weights.

Materials and methods

- Fabric : 100% cotton fabric (Count: 40's X 40's, EPI: 142, PPI : 72 and GSM: 125), ready for dyeing stage, was procured from local process house. All preparatory processes such as desizing, scouring, bleaching, mercerising etc were given in factory itself
- Dyes : Different acid and direct dyes were obtained from M/s Colourtex Ind Ltd, Surat (Gujarat) :
  - C I Acid Blue 158
  - C I Direct Red 81
  - C I Direct Blue 71
- Chitosan : Chitosan samples of different molecular weights were purchased from M/s Marine Chemicals, Cochin (Kerala) and M/s Mahtani Chitosan Pvt Ltd, Veraval (Gujarat). The molecular weights of these samples were determined viscometrically[28].

Table 1 : Specifications of different chitosans

Particulars	Properties	
Supplier	M/s Marine Chemicals, Cochin (Kerala)	M/s Mahtani Chitosan Pvt Ltd, Veraval (Gujarat)
Product Code	C1	C2
DAC Value (%)	89.03	90
Viscosity (cps)	183	22
Molecular weight	6, 54, 127	1, 35, 839

The specifications of different chitosans are given in *Table 1*.

DMDHEU (40%) was obtained from local process house and other chemicals such as acetic acid, sodium acetate (anhydrous), sodium hydroxide, sodium nitrite, methanol etc used were of LR grade of reputed brands.

Depolymerisation of chitosan

Depolymerisation of chitosan was carried out by sodium nitrite. 2 % solution of chitosan (C2) in acetic acid was prepared. Predissolved dilute solution of sodium nitrite was then

added gradually to chitosan solution and stirred for two hrs at 30°C to get desired viscosity level. The depolymerised chitosan was then precipitated out by caustic solution and washed to neutral pH. Chitosans of two different low molecular weights obtained were coded as follows:

Product code	Molecular weight
DC1	71,676
DC2	38,733

Fabric treatment with chitosan

Required amount of chitosan was dissolved in solution containing acetic acid 15 gpl and sodium acetate 10 gpl, and applied to fabric on a padding mangle with wet pick-up of 70% by two-dip-two-nip method. After drying, the fabric was cured in oven at 150°C for 4 mins.The sample was then washed in the following sequence:

Hot wash (Twice) [85°C/20mins] - Alkali wash [Soda ash 10 gpl, MLR 1:50] - Hot wash - Cold wash - Dry.

Dyeing with direct dyes

The fabric sample was dyed with direct dyes with 1% shade at 90°C for 60 mins using dyebath containing 20% Glauber's salt and 5% soda ash. The dyed sample was then rinsed with cold water, air dried and hot pressed.

The dyed samples were evaluated for K/S values and strength on Spectroscan 5100A (Make : Premier Colorscan). The washing fastness of dyed samples was evaluated according to ISO 1.

Dyeing with acid dye

The fabric sample was dyed with acid dyes with 2% shade at 90°C for 60 mins using dyebath containing 1 ml/l acetic acid. The dyed sample was then rinsed with cold water, air dried and hot pressed.

Evaluation of whiteness, yellowness and brightness

The samples were evaluated on Spectroscan 5100A (Make : Premier Colorscan) for whiteness, yellowness and brightness in terms of the corresponding Indices.

Whiteness Index (WI) : 10 deg/D65/ Hunterlab

Yellowness Index (YI) : 2°C/ASTM D 1925

Brightness Index (BI) : 2°C/TAPPI 452/ISO 2470

Crease recovery angle

Crease recovery angles were measured as per AATCC Test Method 66-2003.

Stiffness of fabric (Bending length)

Bending lengths were measured as per standard ASTM D 1388-1996.

Results and discussion

Chitosan is characterised mainly by two variables, namely, degree of deacetylation (DAC value) and the molecular weight. Degree of deacetylation determines the number of free amino groups present in the chitosan macromolecule which, in turn, determines the functionality/reactivity, polarity and water solubility of the polymer. On the other hand, molecular weight determines the strength of its fibre/film and viscosity of its solution. The very high molecular weight and therefore a high viscosity of chitosan solution penetrates less into the fabric structure and hence leads to only surface deposition and alters the fabric feel and appearance. Low molecular weight chitosan often known as chitosan oligomers or chito-oligosaccharides, on the other hand, by virtue of its low viscosity, penetrates to greater extent into the fabric structure. This can offer better durability without much affecting the feel and appearance [29,30]. Therefore, in order to study the chitosan treated cotton textiles, we prepared two different low molecular weight chitosans by depolymerisation.

Various methods of depolymerisation are reported in the literature[4,31,32,33,34,35] such as acid hydrolysis (HCl, HNO_2, etc), free radicals (H_2O_2, $K_2S_2O_8$), enzymatic, radiations (UV, γ rays), ultrasound, microwave, thermal treatments etc. Depolymerisation by acid hydrolysis using nitrous acid (HNO_2) proceeds through deamination reaction with subsequent cleavage of β-glycosidic linkages.

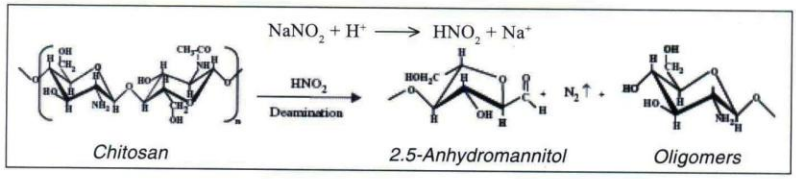
The depolymerisation of chitosan was conducted by nitrous acid hydrolysis method.

Effect of concentration of chitosan on appearance and feel

The viscosity of a polymer solution is also governed by its concentration[36]. The effect of application concentration of chitosan on various physical properties were evaluated and presented in *Table 2* and *Table 3*.

It is observed from *Table 2* that the whiteness and the brightness of chitosan treated fabrics are satisfactory for high molecular weight chitosans but slightly reduced with increase in concentration of chitosan. In general, the whiteness of chitosan is negatively affected due to application of chitosan. The extent of deterioration in whiteness, however, is substantially high in highly depolymerised chitosan i.e. for DC2 at high concentrations. It seems, here, that the excessive depolymerisation by sodium nitrite produces undesired impurities containing aldehyde end groups, which may react with free amino groups to form -N=C bond (Schiff's base) resulting in yellowness[4]. Additionally, the possible liberation of nitric oxide gas from $NaNO_2$ in acidic medium may also enhance the yellowness. A thorough purification of the product may be the remedy.

The fabric stiffness is found to be progressively increased with increase in the concentration and molecular weight of chitosan, as seen from *Table 3*. The



The depolymerisation of chitosan was conducted by nitrous acid hydrolysis method

Table 2 : Appearance of chitosan treated fabric as a function of molecular weight and concentration

Conc (gpl)	C1			C2			DC1			DC2		
	WI	YI	BI	WI	YI	BI	WI	YI	BI	WI	YI	BI
2.5	91.4	3.6	82.4	90.9	3.3	81.6	91.5	3.6	83.4	89.9	3.7	79.8
5.0	91.8	3.6	83.2	90.8	3.4	81.4	91.9	3.6	83.6	89.0	7.4	76.9
7.5	91.4	4.7	82.2	90.4	4.3	80.6	91.5	4.0	82.9	89.2	8.1	76.9
10.0	91.3	4.4	81.9	90.5	4.7	80.6	91.4	4.3	82.6	87.7	9.2	74.2
15.0	90.9	4.9	81.3	90.1	4.5	79.8	91.5	4.7	82.3	86.4	13.5	70.6
20.0	90.2	5.4	79.8	89.2	5.8	77.9	90.3	5.4	79.9	84.1	16.2	66.1

Control : WI = 92.5, YI = 2.6, BI = 84.6

Table 3 : Stiffness of chitosan treated fabric as a function of molecular weight and concentration

Conc (gpl)	Bending Length, cms							
	C1		C2		DC1		DC2	
	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
2.5	2.61	1.76	2.44	1.70	2.33	1.85	2.15	1.60
5.0	2.80	2.10	2.98	2.05	2.58	1.85	2.30	1.71
7.5	3.41	2.55	3.23	2.25	2.68	2.01	2.48	1.86
10.0	4.29	3.03	3.70	2.74	3.05	2.19	2.90	2.00
15.0	4.90	3.23	4.10	3.00	3.39	2.21	3.31	2.38
20.0	5.38	3.53	4.40	3.33	4.06	2.88	3.53	2.68

(Bending length of control sample : Warp = 2.05 cms and Weft = 1.68 cms)

fabric surface was also found to be excessively harsher in case of high molecular weight chitosan. This increased stiffness and harshness may be attributed to the formation of surface coating of stiff film due to very high viscosity of the solution. This property is not desirable in pretreated fabrics but may be beneficial when applied during finishing process, which imparts firmness and body to the fabric. The high viscosity solutions, however, cause difficulties during application in padding mangle.

Absorbency

Rapid and uniform absorbency for any pretreated fabric is indispensable for the better penetration of dyes and chemicals during the subsequent unit operations like dyeing, printing and finishing[37]. Therefore, the effect of chitosan applications on the absorbency was determined, which is shown in *Table 4*.

The absorbency (measured by water drop absorbance time) of chitosan treated fabric is found to be satisfactory. From *Table 4*, it can be observed that average absorbency of high molecular weight chitosan treated fabric decreased slightly with the increase in its concentration; whereas the absorbency of low molecular weight chitosan treated samples is not much affected. The reduction in absorbency in case of former may be due to the formation of rigid film of chitosan over the surface, thus acting as a barrier for the penetration of water.

Table 4 : Effect of molecular weight and concentration on absorbency

Conc of chitosan gpl	Absorbency, seconds			
	C1	C2	DC1	DC2
2.5	5.13	4.54	5.03	7.38
5.0	5.28	4.58	5.03	12.06
7.5	8.44	5.98	6.41	11.43
10.0	12.70	7.20	5.54	9.60
15.0	16.02	7.05	7.05	8.93
20.0	72.28	7.19	7.09	10.13

(Absorbency of control sample : 4.02 secs.)

Dyeing behaviour

Dyeing with direct dyes : Since the structure of chitosan is very much similar to cellulose, it was thought that its treatment may influence the dyeing behaviour of cellulose. In this work, the effect of pretreatment and after treatment of chitosan on direct dyeing of cotton is examined. The washing fastness properties of these samples are als analysed. The effects of chitosan pretreatment on dye uptake, measured in terms of K/S, are shown in *Table 5* and their washing fastnesses are presented in *Table 6*. The effect of chitosan treatment on the shade of dyed fabric and the washing fastness are presented in *Tables 7 & 8* respectively. It is observed from *Table 5* that the dye uptake (K/S), of both the dyes, increased substantially with increase in concentration of chitosan. The dye uptake is also found to be affected by the molecular weight of chitosan.

Table 5 : Effect of chitosan pretreatment on direct dye uptake

Conc of chitosan (gpl)	K/S C I Direct Red 81			
	C1	C2	DC1	DC2
2.5	9.2	9.4	9.4	9.4
5.0	7.9	9.3	10.9	9.9
7.5	9.4	10.9	10.3	11.3
10.0	10.3	11.3	10.9	12.1
15.0	12.8	12.2	11.8	11.4
20.0	14.7	13.5	13.8	12.1
	C I Direct Blue 71			
2.5	8.6	9.6	9.4	9.4
5.0	9.4	11.6	9.8	9.8
7.5	10.6	10.8	9.8	10.1
10.0	13.4	12.4	10.6	13.0
15.0	18.8	15.6	12.2	14.4
20.0	16.6	16.1	13.8	14.4

(Dye : 1% owf, K/S values of control sample : CI Direct Red 81 = 7.7 and CI Direct Blue 71 = 7.4)

Cotton fabric, when introduced in dye bath, acquires negative surface charge and repels negatively charged dye anions, leading to poorer dye exhaustion as found in case of fabric dyed in absence of chitosan. The increased dye uptake due to chitosan treatment may be attributed to the increased dye affinity towards the positively charged amino groups. This charge dissipates the negative surface charge on cotton and drives dye molecules to the fibre. Further, the dye uptake may also have been enhanced due to the dyeability of chitosan itself with direct dyes.

Table 6 shows that the washing fastness of C I Direct Red 81 is marginally improved with the increase in the concentration of chitosan, particularly in case of relatively low molecular weight chitosan treated samples. On the other hand, for the samples treated with high molecular weight chitosan, there is slight reduction in the wash fastness with increase in the treatment concentration of chitosan. However, the effect of chitosan treatment on washing fastness of dyes with good washing fastness viz C I Direct Blue 71, is not altered appreciably.

It is observed from *Table 7* that the colour value of C I Direct Red 81 is little improved whereas that of C I Direct Blue 71 is little decreased due to the chitosan after treatment. This contradictory result may be attributed to the differences in the washing fastness of these dyes. Easily washable Red dye is migrated to a greater extent from the fabric to the chitosan layer during pad application and further during drying. The washing fastness of post dyeing chitosan treated fabrics is improved *(Table 8)*.

- Dyeing with acid dye : Chitosan possesses an amino group in its glucosamine unit, which forms positive charge in presence of acid. This positively charged amino group can form salt linkage with anions. In order to verify this kind of interaction of chitosan, we carried out the dyeing of chitosan treated cotton fabric with acid dyes. The results are presented in *Table 9*.

It is observed from the *Table 9* that the dyeability towards acid dye is substantial in all grades of chitosan. The dye uptake increased with increase in concentration of chitosan. This kind of dyeability can be purely attributed to the binding of acid dye to chitosan by salt linkages. The untreated (control) sample showed merely a tinting effect. Thus, the dyeability toward acid dye can be

Table 6 : Effect of chitosan pretreatment on washing fastness of direct dye

Conc of chitosan (gpl)	Washing fastness ratings C I Direct Red 81							
	C1		C2		DC1		DC2	
	Change in colour	Staining	Change in colour	Staining	Change in colour	Staining	Change in colour	Staining
5.0	2-3	2-3	3	2-3	3	2-3	3	2-3
10.0	3	2-3	3-4	2-3	3	2-3	2-3	3
15.0	2-3	2-3	3-4	3	3-4	3	3-4	3
20.0	2	2-3	3	3-3	2-3	3	3-4	3
	C I Direct Blue 71							
5.0	4-5	3	4-5	3-4	4-5	3-4	4	3-4
10.0	4	3	4-5	3-4	4	3-4	4-5	3
15.0	4	3	4-5	3-4	4	3	4-5	3
20.0	4-5	3	4-5	3-4	4-5	3-4	4-5	3

(Washing fastness ratings of control samples : CI Direct Red 81 : Change in colour = 3 & Staining = 3; CI Direct Blue 71 : Change in colour = 4-5 & Staining = 3-4).

Table 7 : Effect of post-dyeing chitosan treatment on colour depth of direct dyed fabric

Finish Treatment	Conc (gpl)	K/S	
		C I Direct Red 81	C I Direct Blue 71
Control	-	6.6	7.3
C1	5	6.8	7.2
	10	7.2	7.5
C2	5	7.2	6.8
	10	7.5	7.3
DC1	5	6.9	6.8
	10	7.2	7.1
DC2	5	7.2	6.6
	10	6.9	6.6

(Concentration of dye = 1% owm)

Table 8 : Effect of post-dyeing chitosan treatment on washing fastness of direct dye

Finish Treatment	Conc (gpl)	C I Direct Red 81		C I Direct Blue 71	
		Change	Staining	Change in	Staining
Control	-	3	2	4-5	3
C1	5	3	2-3	4	4
	10	3-4	2-3	4-5	4-5
C2	5	3-4	2-3	4-5	4
	10	3-4	3	4	4-5
DC1	5	3-4	3	4-5	4
	10	3-4	3	4-5	4-5
DC2	5	3-4	2-3	4-5	4-5
	10	4-5	3	4-5	4-5

Table 9 : Dyeing of chitosan pretreated cotton with acid dye, C I Acid Blue 158

Conc of chitosan (gpl)	K/S Value			
	C1	C2	DC1	DC2
2.5	1.7	1.5	1.6	2.0
5.0	1.6	2.1	2.3	2.4
7.5	2.3	3.0	2.8	3.5
10.0	3.1	3.8	3.7	3.0
15.0	4.4	4.9	4.9	5.5
20.0	6.1	7.7	6.5	6.3

(Shade : 2% owf, K/S value of control sample : 0.3831)

Table 10 : Wrinkle recovery property of chitosan treated cotton fabric

Conc of chitosan (gpl)	(Crease recovery angle)°			
	C1	C2	DC1	DC2
Control	161	161	161	161
2.5	137	140	140	176
5.0	143	140	160	164
7.5	129	119	152	141
10.0	94	125	138	128
15.0	96	110	127	134
20.0	90	98	116	121

(CRA of control sample = 161°)

taken as one of the characterisation tests for the retention of chitosan on cotton fabric.

Wrinkle recovery property

One of the major drawbacks of cotton textiles is its tendency to crease. Various cross linking agents such as UF, DMU, DMEU, DMDHEU etc resins are employed to overcome this problem. The wrinkle recovery property of chitosan treated fabrics was compared with DMDHEU. The results of this experiment are shown in *Table 10 and Table 11*.

Table 11 : Wrinkle recovery property of DMDHEU treated cotton fabric

Conc of DMDHEU (40%) (gpl)	(CRA)°
Control	161
20	180
40	207
60	215
80	226
100	233

It is seen from *Table 10* that the wrinkle recovery of chitosan treated cotton fabrics is not satisfactory. Rise in application concentration of chitosan has greatly reduced the wrinkle recovery of cotton. However, low concentration of lower molecular weight chitosan application has improved the crease recovery angle. The high molecular weight chitosan is believed to form mostly a surface coating which lowers the possibility of cross linking and therefore cannot contribute to the load sharing phenomenon.

Conclusion

The appearance of cotton fabric, in terms of whiteness/brightness, is affected due to the chitosan application. The stiffness and harshness of chitosan treated fabric also increased with increase in the molecular weight and concentration of chitosan. Chitosan treatment has not affected the absorbency of cotton much. The dyeability of chitosan treated cotton fabrics towards direct dyes is

improved significantly; it is increased with increase in molecular weight and concentration of chitosan. However, the washing fastness of direct dye on chitosan pretreated fabric is only slightly improved, especially for low molecular weight chitosan applications. The effects of post-dyeing treatment for different dyes are different. However, the post-dyeing chitosan treatment, in general, has improved the washing fastness of direct dyed cotton fabric.

Chitosan can, therefore, be taken as a valuable wet processing agent, but yet faces several challenges while exploring its applicability. Therefore, an extensive research in this area is the need of the hour.

References

1 Hirano S, Ullmann's Encyclopedia of Ind Chemistry, 7, Pub : Wiley-VCH (2003) 679-691
2 Oktem T, Col Tech, 119 (2003), 241-246
3 Muzzarelli R A A, 'Chitin Chemistry' in : Salamone, J C (ed), 'The polymeric materials Encyclopedia', Pub, CRC press Inc., Boca Raton Fl, USA (1996), 312-314
4 Harish Prashant K V and Tharanathan R N, Trends in food Science & Technology, 18 (2007) 117-131
5 Giri Dev V R, Neelkandan R, Sudha N, Shamugasundaram O L and Nadaraj R N, Text. Magazine, July (2005), 83-86
6 http://en.wikipedia.org/wiki/Chitosan
7 Kean T, Roth S, Thanou M, J Control Release, 103 (3) : (2005), 643-53
8 http://www.epa.gov/pesticides/biopesticides 'Chitosan, Poly-D-glucosamine (128930) Fact Sheet'. US Environmental Protection Agency (May 2nd 2006), Retrieved on 2006-07-10
9 http://www.ftwa.dot.gov/engineering/geotech Alan Woodmansey (Highway Engineer) (March 19 2002). "Chitosan Treatment of Sediment Laden Water - Washington State I-90 Issaquah Project". Federal Highway Administration. U S department of transportation. Retrieved on 2006-07-10
10 Achwal W B, Colourage, September (2000), 47-48
11 Inamdar M S and Chattopadyay D P, Man Made Text, In India , June (2006), 212-216
12 Achwal,W.B.,Colourage, Aug.(2003) 51
13 Hasebe Y, AATCC Review, 1(11) (2001), 23-27
14 Eom S I, AATCC Review, (3) (2001), 57
15 Knittel D and Schollmeyer E, Melliand English (1-2) (2002), E 15
16 Kh F El Tahlawy, Colourage, XLVI (5) May (1999) 21
17 Chung Y S, Lee K K and Kim J W, Text Res J, 68 (10) (1998), 772-775
18 Zhang Z, Chen L, Ji J, Huang V and Chen D, Text Res J, 73 (12) (2003), 1103-1106
19 Tiwari S K and Gharia M M, AATCC Review, April (2003), 17-19
20 Bahmani S A, East G C and Holme I J, J Soc Dy Col, 116, March (2000), 94-98
21 Dutta P K, Durgabhavani K and Naveen S, Asian Text J, Jan (2001), 57-63
22 Abdel-Mohdy F A, Ibrahim M S and El-Sawy S, J Text A, 66 (5) Jan-Feb (2006), 219-226
23 Patel R, M E Dissertation, Department of Textile Chemistry, Faculty of Tech & Engg, The M S University of Baroda, Vadodara, India, (2006)
24 Kim Y H, Choi H M and Yoon J H, Text Res J, 68(6) June (1998), 428-434
25 Pourjavadi A and Mahdavinia G R, Turk J Chem, 30 (2006), 595-608
26 Pourjavadi A, Barzegar S and Mahdavinia G R, http://www.e-polymers.org, ISSN 1618-7229
27 Gorochovceva N, Kulbokaite R, Juokenas R and Makuska R, Chemija, T-15 (1) (2004), 22-27
28 Knaul Jonathan Z, Kassai Mohammad R, Tam Bui V and Katherine A M Greber, Can J Chem., 76 (11) (1998), 1699- 1706
29 Ha-Soo Seaong, Jae-Pil Kim and Sohk-Won Ko, Text Res J, 69 (7) July (1999), 483-488
30 Deepti Gupta and Komal Saini, Colourage, Vol LV (4) April (2008), 42- 48
31 Hebeish A, Waly A and Aou-Okeil A, J Text A, 65 (5), Jan-Feb (2005), 219-227
32 Kissa E, Text Res J, Aug (1981), 508-513
33 Lee L F, Lee W K, Maskat M Y, Roshli Md Illias, Aziz Suraini A, Kamarulzaman K and Osman H, Pak J Biological Sci, 8 (1) (2005), 73-77
34 Feng Tian, Yu Liu, Keao Hu and Binyuan Zhao, J Material Sci, 38 (2003) 4709 - 4712
35 Stanishlaw Trzcinski, Polish Chitin Soc: Monograph XI, (2006) 103 - 111 'Combined degradation of chitosan'
36 Gowariker V R, Viswanathan N V and Sreedhar Y, 'Polymer Science', Pub: New Age Intarnational Publisher, N.Dehli, (2008), 332 - 362
37 Karmaker S R, "Chemical technology in the pre-treatment processes of textiles", Science and Technology-12, Pub : Elsevier Science B V, Amsterdam (1999), 86.

Bayer MaterialScience ends reduced working hours at German sites

Effective November 1 this year, Bayer MaterialScience (BMS) will be reverting to the standard collectively agreed work week of 37.5 hours at its German sites. At the beginning of February, the company had introduced a reduction in working time and a corresponding pay reduction of 6.7% to combat the effects of the financial crisis. An opening clause in the collective agreement was applied in order to avoid short-time working. With the reintroduction of normal working hours, the rates of pay for some 4,100 employees will return to their normal level.

'The reason for lifting this special arrangement is the improvement in orders. Nevertheless the future business development of our customer industries still remains uncertain,' said Dr Tony Van Osselaer, labour director at Bayer MaterialScience AG. Short-time working would mainly have affected employees in production. 'Thanks to the solidarity of all our employees, this was prevented,' said Thomas de Win, chairman of the central works council of Bayer AG. Managerial employees of Bayer MaterialScience were also affected by the cuts, which in their case included the cancellation of this year's round of pay increases.

Similar measures were also taken at the international sites, adapted in each case to their economic situation.

TECHNICAL ARTICLE

Chitosan and its Versatile applications in Textile Processing

M. S. Inamdar and D. P. Chattopadhyay*

Faculty of Textile Processing, Sarvajanik College of Engineering & Technology, Surat - 395 001 and
**Department of Textile Chemistry, Faculty of Technology & Engineering, The M. S. University of Baroda, Vadodara - 390 001.*

Chitosan, a polysaccharide obtained by the deacetylation of chitin, is a versatile agent used in the primary production of textile fibre, textile auxiliary chemicals and textile finishing agents. Besides its textile applications, it has got a number of other useful uses. In medicine, it is used to make artificial skin and blood vessels, surgical suture, anti-tumour agent, immunity promoter, anti- cholesterol agent etc. In food industry, it can be used as stabilizer and thickener. In daily use chemical industry, it can be used as hair fixer and hair conditioner, and many more. It seems that a number of applications of this polymer are yet to be discovered. Because of the potentiality of this polymer scientists from different fields have been attracted to explore its uses in their respective fields. In this paper, various aspects of chitosan and its textile applications are briefly reviewed.

Key words: Chitin, chitosan, chemistry, properties, applications.

INTRODUCTION

Embellishment of the cloth takes place through various unit operations of wet processing such as desizing, scouring, bleaching, dyeing, printing and finishing. To accomplish these processes, dyes and various chemicals such as acids, alkalies, oxidizing/reducing agents, electrolytes, organic solvents, surfactants, and polymers etc are used. Some of these are retained by the fabric and the excess one are discharged in one or more forms of solid, liquid and gaseous. Many of these dyes and chemicals are toxic and non-biodegradable, and hence deteriorate the ecological balance and the human health.

Ecological considerations, now days, are becoming important factors in the selection of consumer goods, all over the world. The consumers demand not only the right quality product, at right time, at a reasonable price, but also with no harm to ecology during the manufacture as well as in the use. Hence, there has been a constant urge to scientists and industrialists to explore and adopt the substitutes, that are non-hazardous and ecofriendly.The use of natural dyes on textiles has been one of the consequences of increased environmental awareness. Enzymes are commercially available for the processes like desizing, scouring, bleaching, and finishing. Eyes are, today, focused towards biopolymers to minimize the use of hazardous synthetic polymers in textile processing. One such promising example of this kind is CHITOSAN (Pronounced as kite-o-san), which is derived from naturally occurring polymer CHITIN (kite-in).Both chitin and chitosan are biopolymers and are biodegradable, biocompatible with animal and plant tissues, non toxic, and renewable.

Chitin, the precursor of chitosan, is a nitrogen containing polysaccharide and is second most abundant biopolymer after cellulose. It is widely distributed in the shells of crustaceans such as crabs, shrimps, lobsters etc as well as in the exoskeleton of marine zoo-plankton, including coral, jellyfish and squid pens. About 20-40% chitin is present in the exoskeleton of these animals. It is also present in smaller quantities in insects such as butterflies, ladybugs, and the cell walls of yeast, mushrooms and other fungi. But since the crustacean shells (crabs etc) are waste products (now byproducts) of food industry, these are commercially employed for production of chitin and chitosan.It is believed that at least ten gigatons (10^{13} Kgs.) of chitin are synthesized and degraded and it is also estimated that over 1,50,000 tons of chitin is available for commercial use annually[1,2,3].

BRIEF HISTORY OF CHITIN AND CHITOSAN

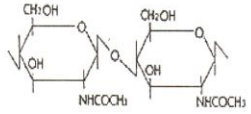
Prof. Henri Braconot, Director of Botanical Garden in Nancy (France) in 1811, first isolated a fraction from the cell walls of mushroom, which he called FUNGINE. Later in 1823, Odier discovered that this compound is also one of the major

constituent of the exoskeleton of insects and then he re-named as CHITIN (meaning tunic or envelope in Greek).Prof.C.Rouget in 1859, prepared a compound from chitin by treatment with concentrated caustic solution .This compound was then named as CHITOSAN by Hoppe- Seiller in 1894.However, the existence of chitosan in nature was discovered in 1954 in the yeast Phycomyces blakesleeanus.

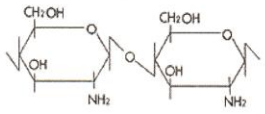
Over past decades, researchers in Korea, Japan, Europe and USA have tested chitin and chitosan in biomedical applications. In Japan, chitosan was first used for waste water treatment to absorb grease, oils, heavy metals and other potentially toxic substances. Researchers claim that a tooth paste made from crab's shell could cut dental infections and reduce the number of visits to dentists [3, 4].

CHEMISTRY OF CHITOSAN

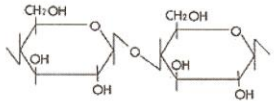
Chitosan [$(C_6H_{11}O_4N)_n$] is a polysaccharide composed of a linear (1-4) linked 2- amino-2-deoxy-β- d- glucan (i.e. β- d-glucosamine) in the chair $^4C_1$ conformation. It is derived by deacetylation of chitin i.e. (1-4) linked 2-acetaamido-2-deoxy-β- d- glucan (i.e. N-acetyl- β- d-glucosamine).Indeed, it is a copolymer of N-acetyl-glucosamine and glucosamine units. The structure of chitosan is very much close to that of cellulose except the hydroxyl group in C (2) of cellulose is being replaced by amino group in chitosan. This is evidenced by I.R. and ^{13}C NMR spectroscopy. The average molecular weight determined by the viscosity measurement methods is of the order of $5x10^5$.The structures of chitin, chitosan and cellulose are as below.



Chitin



Chitosan



Cellulose

Chitosan mainly occurs in two molecular conformations, namely (i) as extended two-fold helix and (ii) as extended eight-fold helix. The eight fold helix conformation transforms into two-fold helix under high humidity .No ordered conformation, however, is present in the aqueous acidic solution. The molecular flexibility increases with increase in deacetylation, increase in ionic strength in the solution and increase in temperature [5, 6, 7, 8, 9, 10, 11, 12].

PRODUCTION OF CHITOSAN

Chitosan can directly be isolated from some fungi, mainly, Phycomyces blakesleeanus (yeast), Zygomycetes etc species. However, the yield is too low. To-date, chitosans have been produced commercially by the alkaline deacetylation of crustaceans chitins.

The crustacean shells mainly consist of chitin (20-30%), proteins (30-40%), Calcium Carbonate (30-50%), lipids and traces of pigment. The proteins are removed by treatment with dil.sodium hydroxide (about 10%) at about 85° C to 100° C or digested enzymatically by proteases or micro-organism. The shells are then dematerialized to remove calcium carbonate by the treatment with dil.hydrochloric acid (about 10%) at room temperature .Lipids are extracted by soaking in organic solvents such as acetone or ethanol. An oxidative bleaching treatment with hydrogen peroxide or sodium hypochlorite is also given to obtain a white powder.

Squid pens are also the potential source of chitin and chitosan. Squid-pens are removed from the squid during processing and are currently regarded as 'waste' so the raw material is cheap. Since, the squid pens are very low in calcium; the acid extraction step is not required. This inturn reduces the cost and acid hydrolysis of chitin. Therefore, comparatively cheaper and better quality chitin can be produced.

Conversion of chitin into chitosan involves the deacetylation process, which is a harsh treatment usually performed with concentrated sodium hydroxide solution. Chitin flakes are treated in suspension with aqueous 30 - 60% caustic solution at 80 - 120°C with constant stirring for 4 - 6 hours and this treatment is repeated for once or more times for obtaining high amino content product. To avoid depolymerization due to oxidation, sodium borohydrate is added. Deacetylation of chitin can also be done enzymatically.Here.powdered chitin is treated with N-deacetylase (EC 3.5.1.41) or with microbes which secrete N-deacetylase. The enzymatic method yields chitosan with low degree of N-acetylation and low degree of polymerization.

The degree of acetylation of chitosan may be determined by C:N ratio (by elemental analysis) , by ^{13}C NMR ,by ^{15}N NMR, by I.R. Spectroscopy, by colloidal titration and by pyrolysis - gas chromatography. In general, chitosans have nitrogen content higher than 7% and degree of acetylation lower than 0.40 [4, 13, 14, 15, 16, 17, 18, 19].

PROPERTIES OF CHITOSAN

Chitosan is a white fibrous material (also available as beads and membranes), produced in different grades according to the degree of deacetylation (D.D.) and the molecular weight. Various factors such as source of chitin and processing parameters while conversion of chitin into chitosan determines the grades of chitosan.

Chitosan being a primary aliphatic amine, it can be protonated by selected acids (p^{ka} of chitosan= 6.3). It is insoluble in water, organic solvents and alkalies, but is soluble in or-

ganic acid solutions. In aqueous solutions, above certain polymer concentration, intermolecular interactions lead to the formation of associations thus exhibiting properties .The viscous solution shows Newtonian flow.

Under particular conditions, chitosan can give highly hydrophilic water swellable hydrogels. One of the simplest ways to prepare chitosan gel is to treat chitosan acetate solution with carbamide.The gel formation is also promoted by adding cross linking agents or organic solvents.

Chitosan also possesses film formation property. The films are mostly flexible with smooth and shiny surface. The quality of film depends on the source from which the precursor 'chitin' is obtained. The films of quid-pen chitosan are clearer and rigid than that of crab and cray fish chitosan [11,12,14,20,21,22].

Chitosan has two hydroxyl functional groups at 3rd and 6th carbon atoms and one amino functional group on 2nd carbon atom. The amino functional group imparts strong positive charge to chitosan which allows it to bind negatively charged surfaces such as skin, hairs, textiles etc.The cationic nature of chitosan also helps to bind cholesterol and clotting of R.B.C. Further, this amino group gives usual chemical reactions such as acetylation, quaternization, reactions with aldehydes and ketones (to give Schiff's base) alkylation, grafting, chelation of metals etc . Chitosan is readily depolymerized by acidic sodium nitrite to give oligosaccharide. The hydroxyl functional groups also give various reactions such as o-acetylation, H-bonding with polar atoms, grafting etc [23,24,25,26,27,28,29,30].

Chitosan also exhibits several valuable inherent properties such as anti bacterial, anti fungal, anti viral, anti acid, anti ulcer, non toxic, non allergenic, total biodegradability etc and hence finds wide applications in diverse fields such as waste water treatments, food, medical, biotechnology, agriculture, cosmetics, pulp & paper, plastic and textile industries. Over 250 applications are known at present [3,31,31,33,34,35].

Some of the applications of chitosans in the area of textiles are discussed in the following sections.

CHITOSAN FIBRES

Owing to the linear structure, chitosan exhibits fibre forming property.Chitosan filaments also known as crabyon (crab + rayon) are produced by wet spinning method. Chitosan is dissolved in acetic acid solution and then extruded through the spinneret into a caustic co-agulation bath to obtain a regenerated fibre. However, such fibres have poor wet strength (tenacity 2.0 gpd) .Investigations have shown the improved tenacity of up to 4.4 gpd by incorporation of surfactants into the coagulation bath. Such fibres find use in the production of textiles having antimicrobial, antithrombogenic, hemostatic, deodorizing, moisture controlling, and non allergenic properties which are inturn used as bandages for wound- dressing, as sutures, as perfume releasing fabrics.

A composite material of chitin/chitosan and cellulose are produced by mixing powder chitin/chitosan with viscose pulp and then wet spun.These fibers have high moisture keeping property than cellulosic fibres and have dyeability towards direct and reactive dyes. These fibres are used as textile materials for under wears, socks, etc as these keep skin from drying. At the same time, these give velvet touch and no irritation to skin .Therefore; clothes made up of these fibres are excellent for babies and old aged people who have weak and sensitive skin [3, 10, 35, 36, 37, 38].

APPLICATIONS OF CHITOSAN IN TEXTILE PROCESSING

DYEING

Cotton and other cellulosic fibres, conventionally, are dyed with direct, reactive, vat, reactive, azoic etc dyes, which are anionic in nature. Cotton also acquires negative surface charge when immersed in dye baths of above dyes leading to repelling action to them. To dissipate this -ve surface charge and to facilitate the dyeing, large amount of electrolytes such as common salt or Glauber's salt are added into the dye bath. These electrolytes and unexhausted dyes add to the pollution load when discharged through effluents. Such high salt dissolved water can neither be useful for agriculture purpose nor be recycled for industrial uses. Moreover, the available technique of reverse osmosis (R.O.) to reduce the T.D.S.is not yet economically viable. Thus attempts have been made to adopt salt free and alkali free dyeing by cationization of cotton by treatment with glycidyl trimethyl ammonium chloride, N, N-dimethyl azetidinium chloride (DMAAC), N-methylol acrylamide (NMA), chloropropionyl chloride (CPC) etc. However, the question of ecological aspects arises here too. As a solution, modification of fibre with chitosan could be a best option.

The fabric is pretreated with chitosan by pad-dry-cure method using cross linking agents such as polycarboxylic acid (e.g. butane tetra carboxylic acid or citric acid) or N-methylol compounds (e.g. DMDHEU). Investigations have shown several valuable results such as: increased dyeability of cotton toward direct and reactive dyes in absence of salt, dyeability toward acid dyes, elimination of colour difference between matured and immatured cotton, coverage of neps etc.It is believed that, chitosan acts as built-in catalyst of reactive dyes in question with hydroxyl groups of cotton and chitosan. Very recently, it has been revealed that a complete salt-free dyeing of cotton with a lot of saving in the quantity of dyes is possible by simple modification of chitosan and its application to cotton material [12,20,28,39,40,41,42].

PRINTING

Chitosan solution on drying gives a colourless, transparent

and flexible film having smooth surface. These films are wash fast when fixed on fabric by thermofixation. Further, chitosan exhibits thickening properties. Thus, by virtue of these properties, chitosan can be used in pigment printing to replace the conventional synthetic binders which are based on styrene-butadiene, styrene-acrylates, or vinyl acetate-acrylate co-polymers [11,43].

WOOL TREATMENT

Wool, due to its scaly structure, exhibits felting problem as a result of frictions arising during various wet processing operations. The penetration of dyes and chemicals through the fibres/yarns is, thus, hindered. Conventionally, the felt formation is prevented by descaling process with treatments such as chlorine, enzymes (protease) etc.The chlorine treatment, however, is not ecofriendly and causes tendering of the fibres.Where as, the second one requires exact control of parameters and is not enough to fulfill the woolmark requirements. Recently, investigations have shown reduced felting of wool when treated under plasma. This process, however, is not economically viable due to prolong treatment time and high cost.

Treatment of wool with chitosan has been found to minimize this felting problem. The bio-adhesive and cationic nature of chitosan enables it to form a strongly adhered film on individual fibres and prevent their entanglements. The extent of adsorption and uniformity of distribution of chitosan onto the fibre can be increased by increasing the wettability and anionic character of fibre. Alkaline peroxide pre-treatment or oxidative plasma treatment creates new anionic groups such as sulphonate and carboxylate, and improves the wettability of wool fibre and hence the binding power of chitosan. However, such degradative treatments lead to considerable weight loss and damage to the fibre. Treatment of wool with a surfactant containing anionic groups can lead to higher pick up of chitosan causing no damage to the fibre. A combination of controlled enzymatic treatment followed by chitosan treatment can also give satisfactory antifelting effect. Further, these treatments have also shown increased shrink resistance and dyeability of wool towards reactive dyes [11,44,45,46,47].

POLYESTER TREATMENT

Besides several useful essential properties, polyester suffers from one serious drawback of hydrophobicity and consequently the static charge built-up problem. This static electricity is mostly responsible for dust/dirt attraction, sticking of clothes to human skin, increased fibre contamination during textile finishing, overlapping of fabric heat setting on stenter, malfunctioning of electric devices, sparks and ignition of its materials etc. To dissipate such static charges, the fibre surface is coated with an antistatic agent, which is mostly synthetic hydrophilic resins, by simple pad-dry-cure method. However, the effect is not durable. An ecofriendly and durable antistatic finish can be obtained by the treatment of polyester with chitosan. Chitosan has the advantage that it shows high moisture regain even in low relative humidity and does not swell much in water. The finish is more stable on polyester that has under gone a caustic reduction treatment. Here cross linking of chitosan takes place by reacting chitosan-NH_2 group with carboxyl end group of polyester that are generated by caustic reduction process [48,49].

ANTICREASE FINIHING

The creasing problem of cotton is well known, which is attributed to the presence of free hydroxyl groups in the fibre molecules. The creasing problem is minimized by cross linking these free hydroxyl groups on adjacent molecules in the fibre using a suitable cross linking agent such as N-methylol compounds (UF, DMDHEU etc resins). However, these finishing agents suffer from one serious drawback of release of toxic free formaldehyde. As an alternative, on formaldehyde cross linking agents such as citric acid, butane tetra carboxylic acids (BTCA) etc are recommended. Among these, BTCA is most effective cross linking agent; but the cost is very high. Citric acid, although cheaper, is less effective and has drawback of yellowing problem due to the formation of unsaturated polycarboxylic acid (due to dehydration of citric acid). To counteract this yellowness, additives such as hydroxyethyl amines, borates or polyethylene glycols to citric acid bath are recommended. However, the process is still less effective.

The crease recovery power of citric acid can be improved satisfactorily by the incorporation of chitosan in presence of sodium hypophosphite monohydrate (SHP) to the citric acid bath. Here, the esterification reaction not only occurs between citric acid and cellulose but also between citric acid and hydroxyl groups of chitosan and the free carboxylic groups can also react with amino groups of chitosan by salt linkages. Low molecular weight chitosan (obtained by controlled oxidative degradation by sodium nitrite) at low concentrations have shown improved wrinkle recovery without deterioration in whiteness and strength of fibre [12, 20,28,35,50,51].

ANTIMICROBIAL FINISHING

The conventional temporary wound dressing used with antimicrobial cream and ointment is time consuming and patients feel pain because of the frequent replacement of wound dressing. Therefore, the method of drug delivery system has been accepted for full-thickness skin wound care and the antimicrobial agent impregnated wound dressings are proven effective in controlling bacterial invasion through a porous matrix. However, the use of conventional antimicrobial agents such as organo-metallics, phenols, quaternary ammonium salts, organo silicones etc are not desirable due to their toxic nature. In this regard, drug impregnated polyelectrolytes wound dressings composed of chitosan and

sodium alginate in sponge form are used. The non toxic, antifungal, antiviral and antimicrobial nature of chitosan accelerate the wound healing and the sodium alginate provides the moist wound atmosphere which promotes healing and epidermal regeneration.

The antimicrobial property of chitosan is attributed to the primary amino group at C-2 position of glucosamine residue. The effect is more enhanced when the amino group is protonated or quaternized. The protonised amino groups block the protein sequences of micro-organisms, thus inhibiting further proliferation. Chitosan binds to the anionic surface of microbe cell wall and disrupt it and alter its permeability. This results material to leak out of bacterial cells causing in cell death. Chitosan also binds to DNA inside the cell inhibiting mRNA and hence protein synthesis.

Also, the antimicrobial treatment of chitosan can be done on various textiles such as cotton, wool etc for preservation and antifungal effects. It also helps odour reduction and perspiration bonding. The antimicrobial finish of chitosan (dissolved with acetic acid) on cotton fabric can be applied by usual pad-dry-cure technique. Incorporation of cross linking agents such as citric acid, glutaric dialdehyde, glyoxal, or DMDHEU etc enhance the chitosan uptake on the surface of cotton fabric with good durability to washing [3,20,35,52,53,54].

EFFLUENT TREATMENT

Textile process houses discharge huge quantities of dyes and chemicals through the effluent. Conventionally, the effluent water is processed by treatment with lime & ferrous sulphate system and/or synthetic polyelectrolytes mostly based on polyacrylamide. Colouring matters and some organic chemicals are flocculated by this method but the TDS value due to inorganic salts is significantly increased leading to increased pollution load. Treating waste water using "greener" methods has become an ecological necessity. The ecofriendly polysaccharide, chitosan, has proved to be the best alternative. Being cationic in nature, chitosan has high affinity for wide range of dyes and other negatively charged particles and flocculate them. Various chitosan polyelectrolytes obtained by reaction polyanions, acidic polysaccharides, and some acidic proteins can be used for effluent treatments [2,11,14,55,56].

REFERENCES

1 H.K. No, and S.P. Meyers, J. Aquatic Food Product Tech., 4 (1995) 27-52.

2 R.A.A. Muzzarelli, 'Chitin Chemistry' in: J.C. Salamone, (ed), "The polymeric materials Encyclopedia", Pub. CRC press Inc., Boca Raton Fl, USA (1996) 312-314.

3 S. Hirano, 'Chitin and Chitosan', Ullmann's Encyclopedia of Industrial Chemistry, Pub. Wiely-VCH, 6 (2003) 679-691.

4 L.L. Davis and S. Bartnicki-Garcia, Biochemistry, 23(6) (1984) 1065-73.

5 Y. Inoue, 'NMR determination of degree of acetylation' in: R.A.A. Muzzarelli, and M.G. Peter, (eds), "Chitin Handbook", Pub. Atec, Grottammare, Itali (1997) 133-136.

6 M.G. Peter, R.A.A. Muzzarelli and A Domard (eds), "Advances in Chitin Science", Univ. Potsdam, 4 (2000).

7 G.A.F. Roberts, "Chtin Chemistry", Pub. Macmillam Press, London (1992).

8 Mukesh Kumar Singh, Man Made Textiles In India, 14 (7) (2002) 279-286.

9 K. Ogawa, Agric.Biol.Chem. 55 (1991) 375.

10 Vivek L. Singh, Asian Tex. J. (1-2) (2005) 65.

11 N. Sekar, Colourage, (7) (2000) 83.

12 Kh.F.El. Tahlawy, Colourage, (5) (1999) 21.

13 H.M. Cauchiel, G. Murugan, J.P. Thome and H.J. Dumont, Hydrobiologia, 359 (1997) 23

14 R. Shepherd, S. Reader and A. Falshaw, Glucoconjugate J. 14 (1997) 535-542

15 R.H. Hackman and M. Goldberg, Aust.J.Biol.Sci, 18 (1965) 935-946.

16 T. Sannan, K. Kurita, Y. Iwakura, Makromol. Chem. 176 (1975) 1191.

17 S. Aiba, Int.J.Biol.Macromol. 13 (1991) 42.

18 J.G. Domszy, G.A.F. Roberts, Macromol Chem. 186 (1985) 1671.

19 H. Terayama, J. Polym. Sci. 8 (1952) 243.

20 Tulin Oktem, Col. Tech 119 (2003) 241.

21 F.L. Mi, S.S. Shyu, C.Y. Kuan, S.T. Lec, K.T. Lu and S.E. Jang, J. Appl. Poly. Sci. 74 (1999) 1861.

22 X. Qu, A. Wirsen, Wirsen and A.C.Albertsson, J. Appl. Poly. Sci. 74 (1999) 3193.

23 M. Yalpani (ed) "Polysaccharides: Synthesis, Modifications and Structure/Property Relations", Pub. Elsevier, Amsterdam, (1988).

24 J. Dutkiewicz, J. Macromol.Chem. 20 (1983) 877.

25 E. Kokufuta, Y. Hirai, I. Nakamuza, Macromol. Chem., 182 (1981) .1714

26 I.D. Hall, M. Yalpani, Biopolymers 20 (1981) 1413.