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

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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 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 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^{+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. Either 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 required the 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

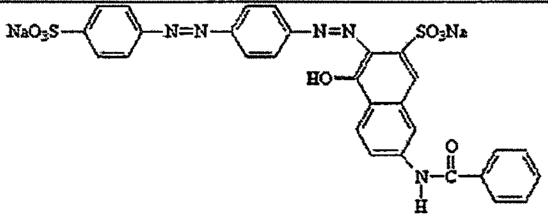
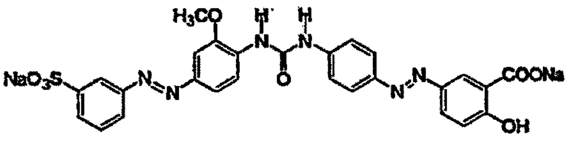
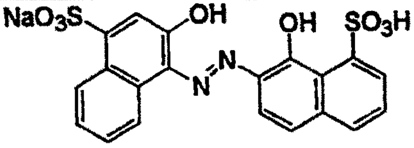
5.2.1 Fabric

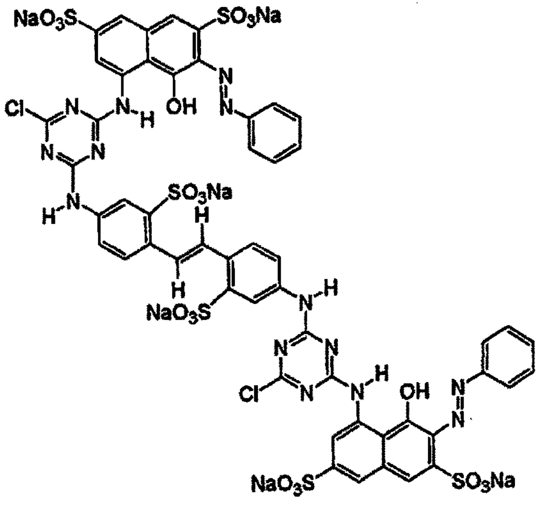
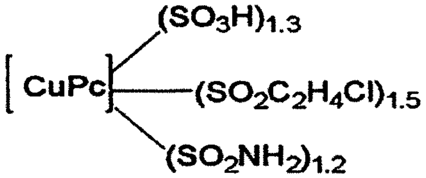
100% grey cotton fabric (warp and weft count 40s) was procured from Mafatlal Industries Ltd, Nadiad, Gujarat State and scoured/ bleached fabric as described in section 2.2.1(chapter 2).

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.	 $[CuPc](SO_3H)_{1.3}(SO_2C_2H_4Cl)_{1.5}(SO_2NH_2)_{1.2}$
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].

$$\text{Calcium content, mg/L (as Ca}^{+2}\text{)} = \frac{ml\ of\ EDTA\ titrant \times 1 \times 1000}{ml\ of\ sample\ taken\ for\ titration} X 0.40 \qquad \textbf{(5.1)}$$

[1 ml of 0.02N EDTA ≡ 1 ml of $CaCO_3$]

Chelation efficiency in terms of sorption of Ca^{+2} ions by chitosan (mg/g) $= \frac{I_0 - I_F}{M}$ **(5.2)**

Chelation efficiency in terms of Ca^{+2} ions removal from water (mg/L) $= I_0 - I_F$ **(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)

$$\begin{array}{l}\text{Chelation efficiency in terms of sorption} \\ \text{of Cu(II) ions by chitosan (mg/g)}\end{array} = \frac{I_0 - I_F}{M} \qquad \textbf{(5.5)}$$

$$\begin{array}{l}\text{Chelation efficiency in terms of} \\ \text{copper ions removal from water (mg/L)}\end{array} = I_0 - I_F \qquad \textbf{(5.6)}$$

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.

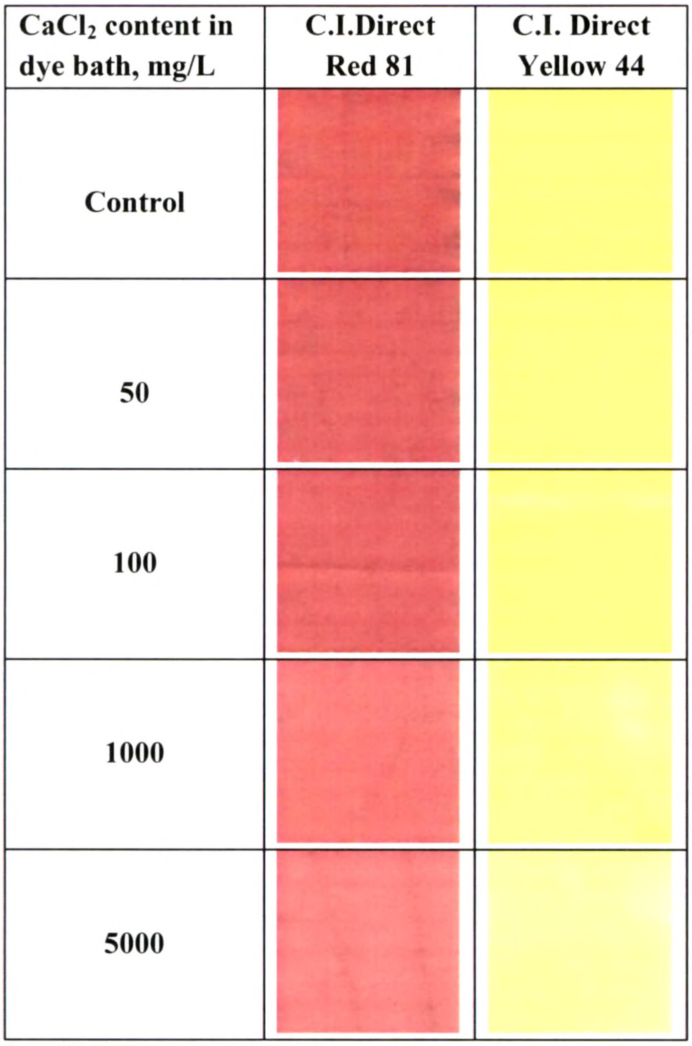
5.2.14 Purification and strength determination of direct and acid dyes

Commercial grade anionic dye (i.e. direct dye or acid dye) was mixed with dimethyl formamide (DMF) at 60°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°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.

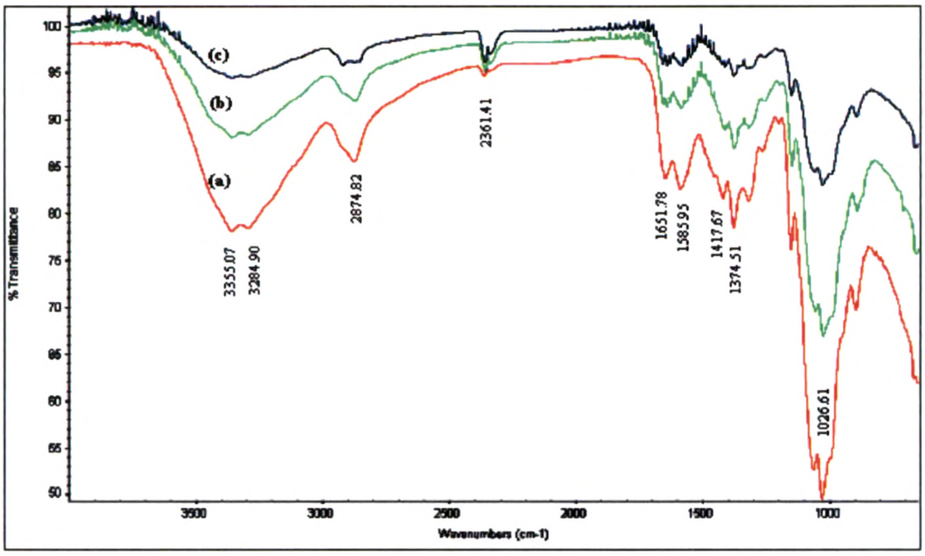
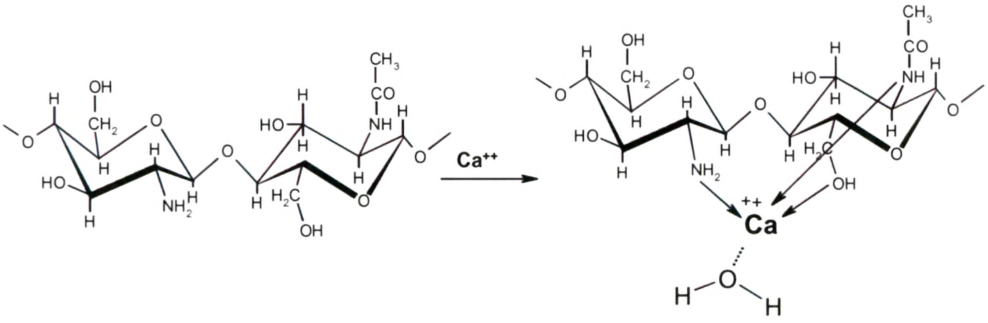


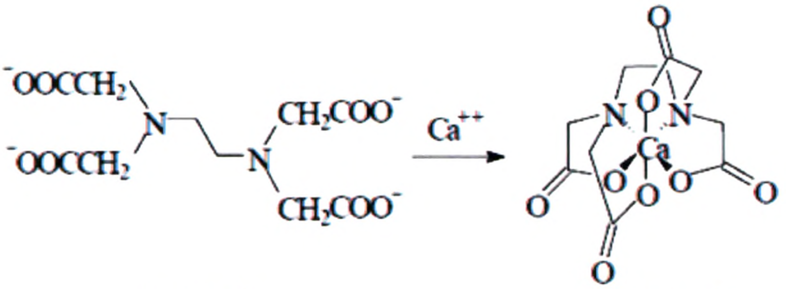
Figure 5.2 FTIR spectra of CHT and CHT-Ca complex residues: (a) CHT, (b) CHT-Ca, treatment time, 24h and (c) CHT-Ca, treatment time 96h

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%

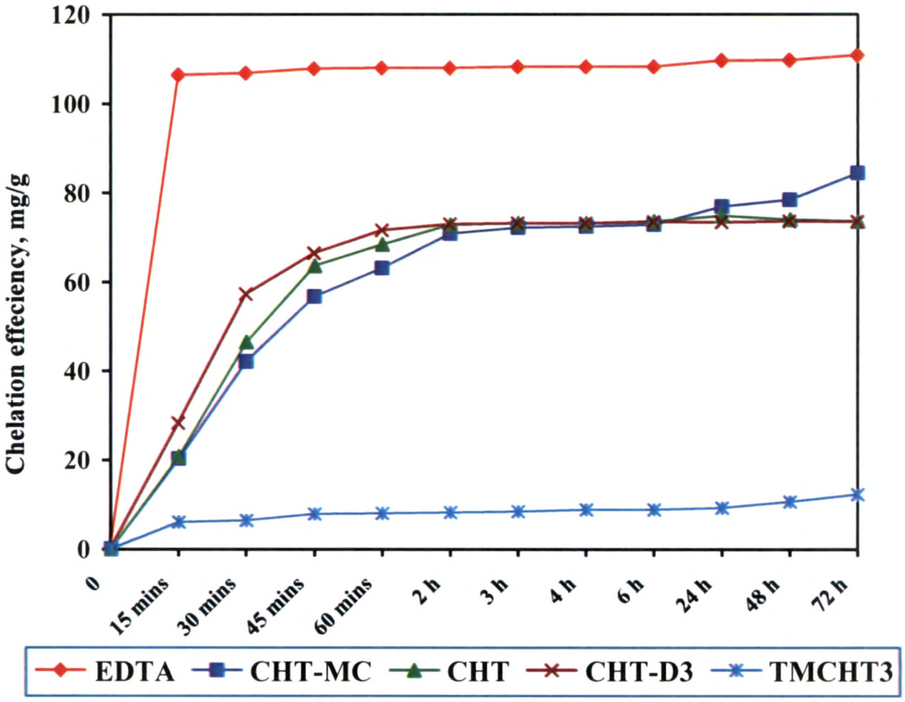
Table 5.6 Effect of treatment time on extent of chelation of Ca^{+2} ions by different chelating agents

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 goes 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

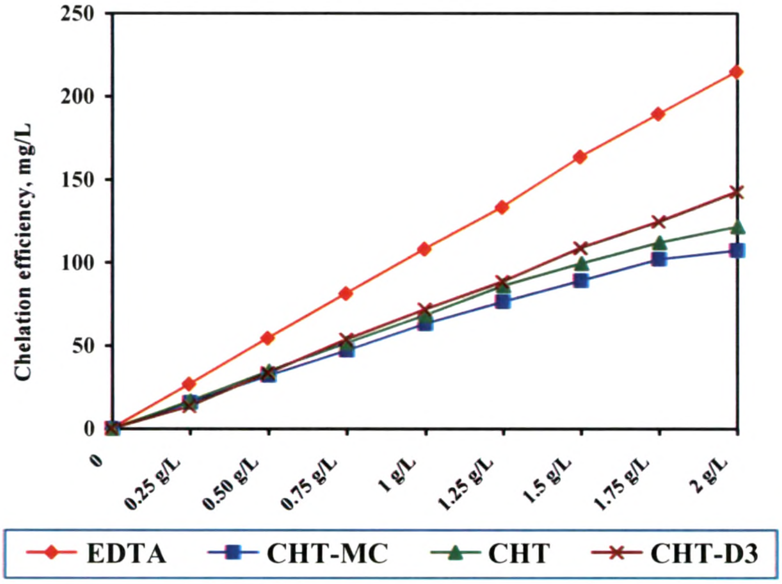
Conc, g/L	**Residual Ca^{+2} ions content in water (I_F, mg/L) after treatment with:**			
	Na_4EDTA	**CHT-MC**	**CHT**	**CHT-D3**
0.25	223.20	234.40	233.20	236.61
0.50	195.60	218.16	215.36	216.52
0.75	168.80	203.07	198.40	196.37
1.00	142.00	186.93	181.60	178.41
1.25	116.80	173.76	164.00	161.57
1.50	86.56	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

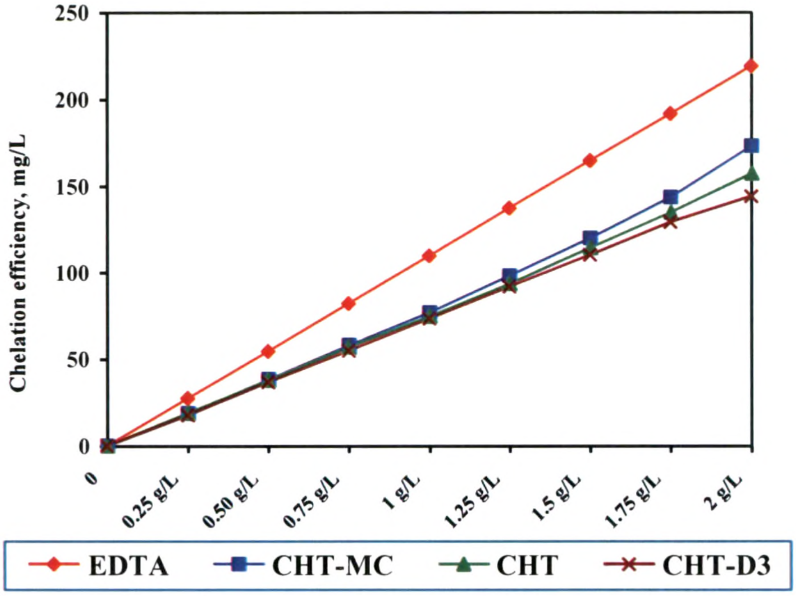
Conc, g/L	**Residual Ca^{+2} ions content in water (I_F, mg/L) after treatment with:**			
	Na_4EDTA	**CHT-MC**	**CHT**	**CHT-D3**
0.25	222.58	231.21	230.93	232.32
0.50	195.52	211.55	212.22	213.26
0.75	167.94	191.93	193.12	195.17
1.00	140.40	173.10	175.20	176.60
1.25	112.78	151.92	156.48	158.27
1.50	85.41	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 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 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 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

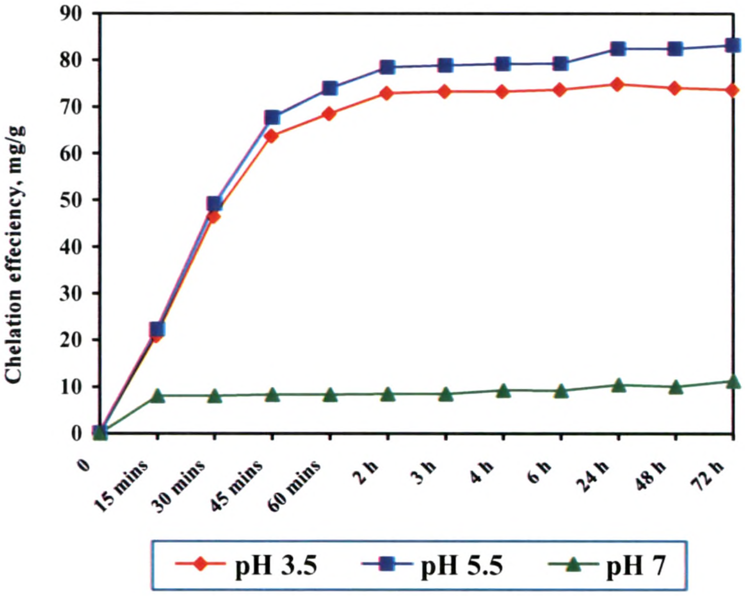
Treatment time	**Residual Ca^{+2} ions content in water (I_F, mg/L) after treatment with CHT at:**		
	pH= 3.5 (Homogeneous system)	**pH= 5.5 (Homogeneous system)**	**pH= 7 (Heterogeneous system)**
15 min	229.20	227.76	242.00
30 min	203.60	200.80	242.00
45 min	186.40	182.40	241.76
60 min	181.60	176.16	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

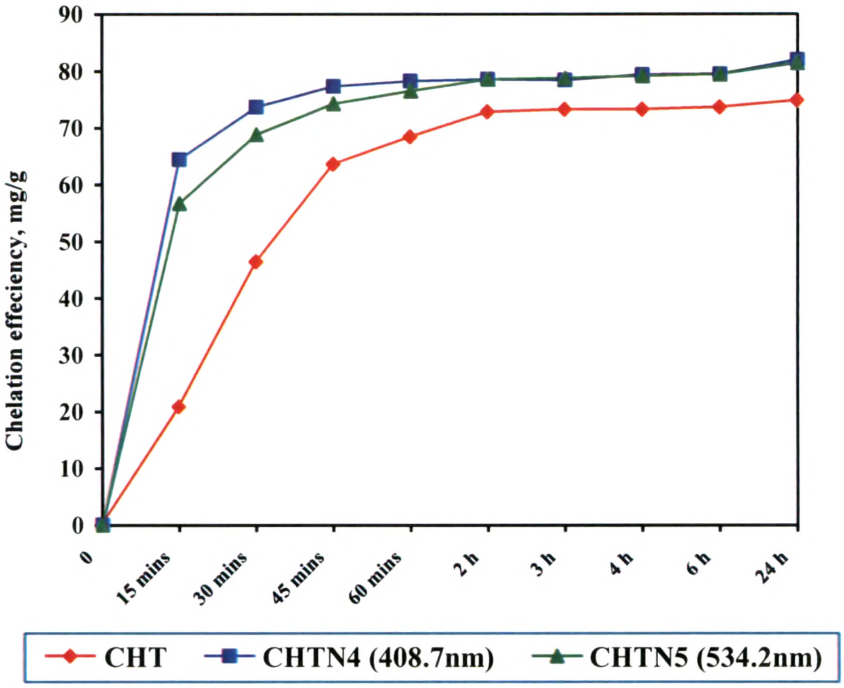


Figure 5.7 Effect of particle size on chelation efficiency of CHT for calcium ions

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

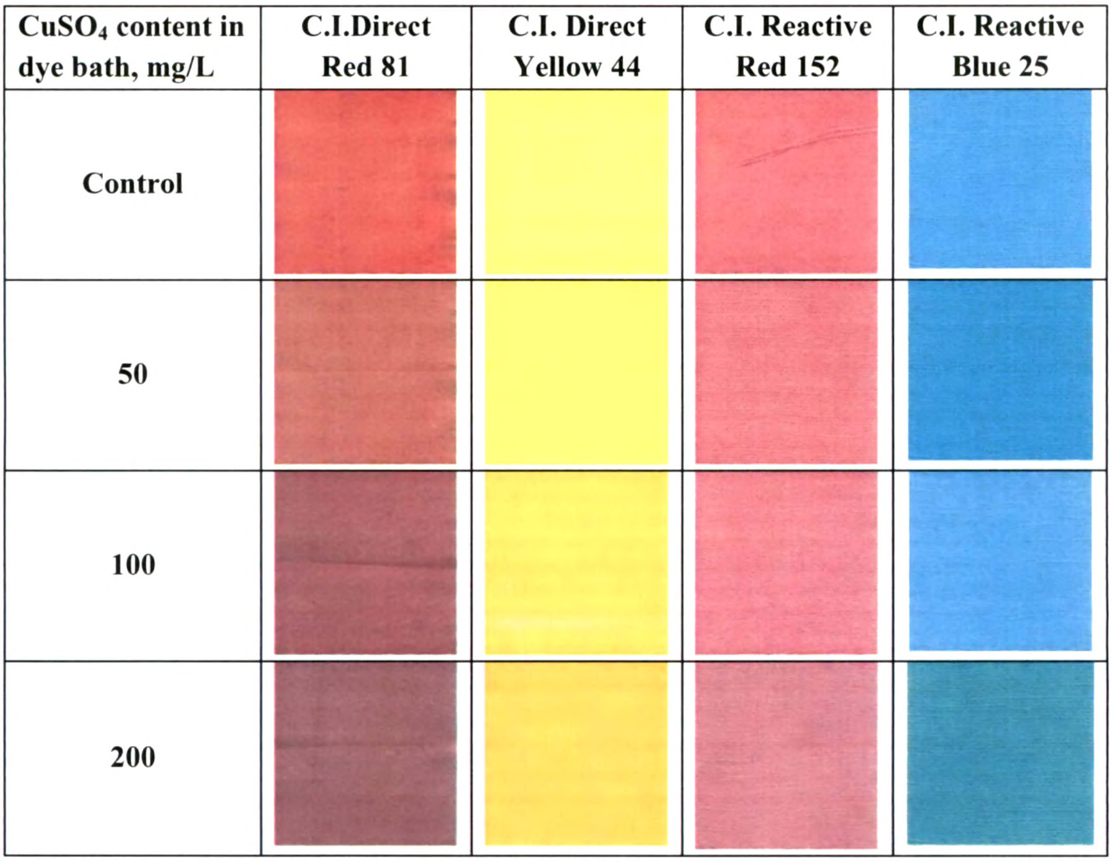
CuSO$_4$ content in dye bath, mg/L	**C.I. Direct Red 81**				**C.I. Direct Yellow 44**			
	K/S	**Value of colour spacing coordinate**		**Look**	**K/S**	**Value of colour spacing coordinate**		**Look**
		a	**b**			**a**	**b**	
Control	8.99 *(100)*	46.34	11.76	Bright	5.35 *(100)*	2.33	74.55	Bright
50	7.90 *(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.

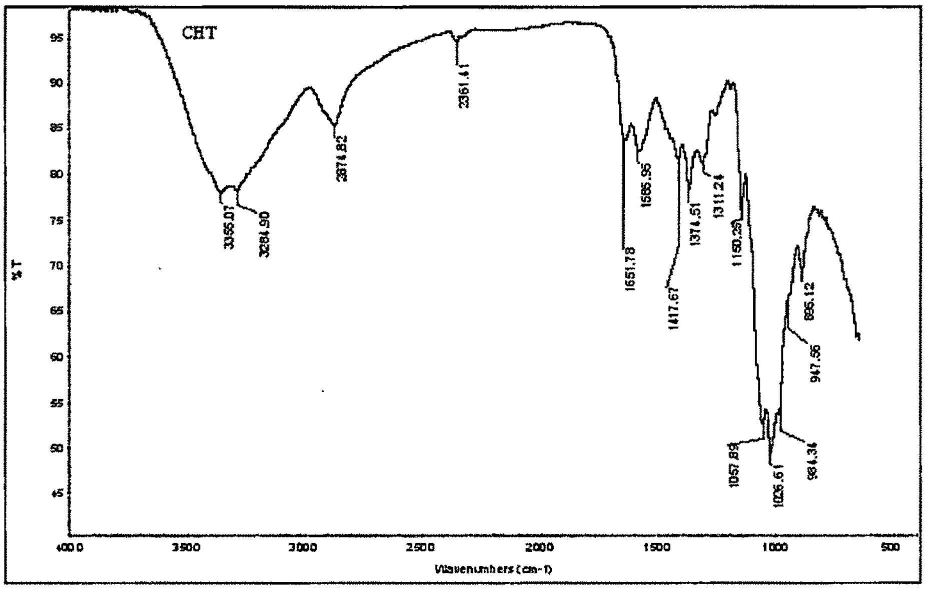


Figure 5.9 FTIR spectrum of CHT

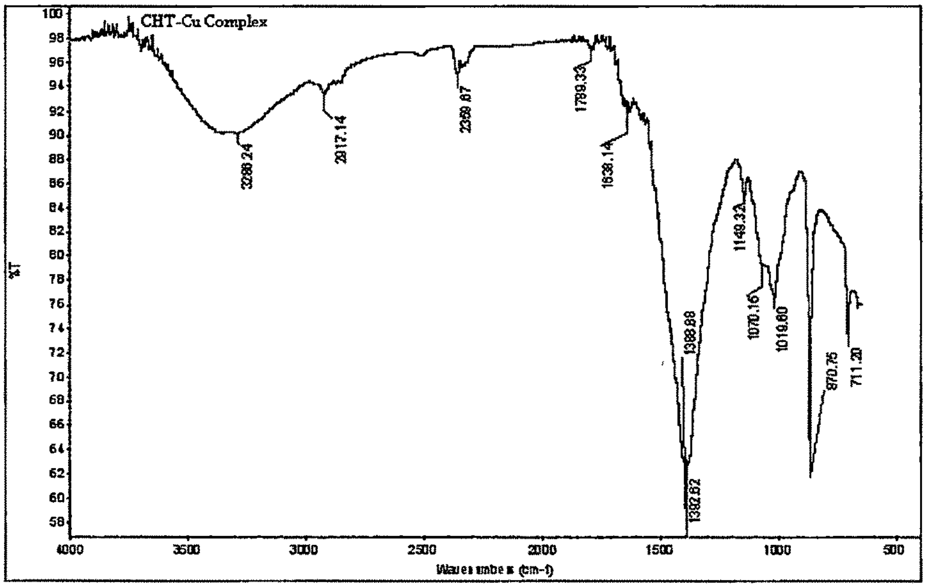
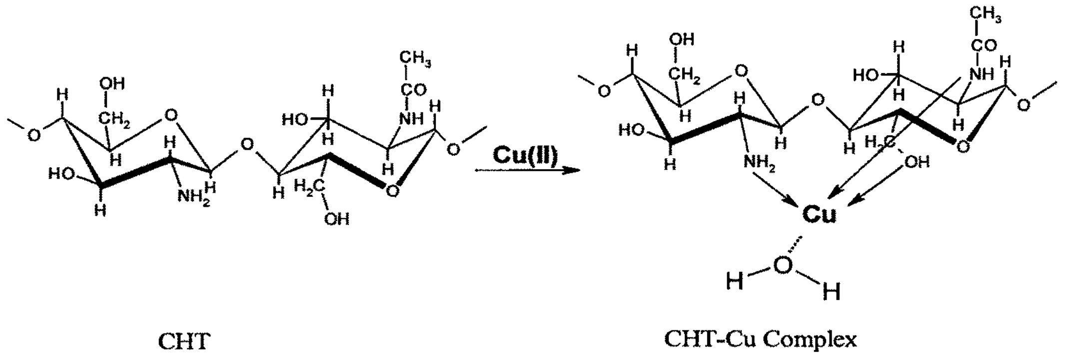


Figure 5.10 FTIR spectrum of CHT-Cu complex residue

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 °C 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 the sorption 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

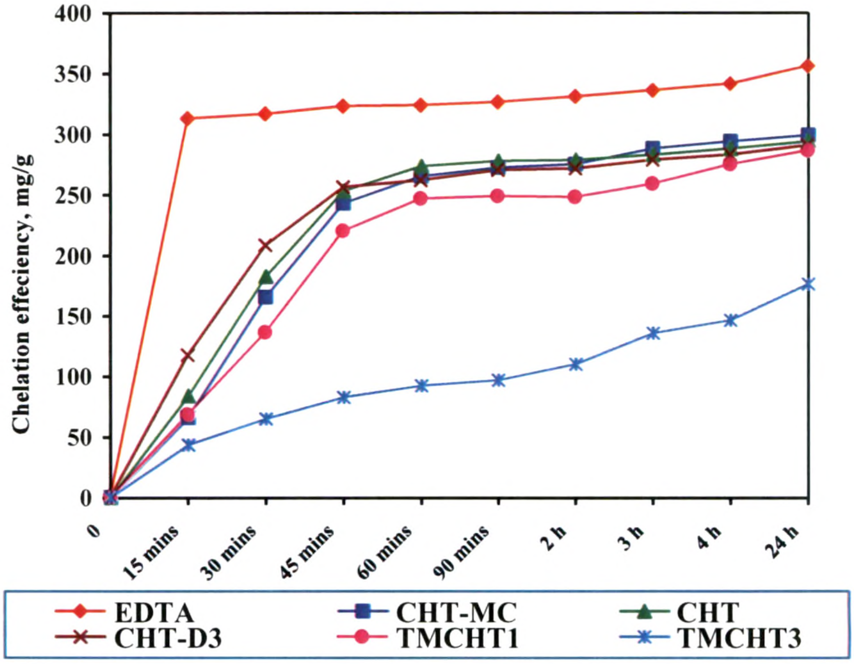
Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; CHT-D3=38,733; DQ: TMCHT1= 13.41%, TMCHT3= 50.92%, Conc of chelating agent 1g/L, Initial conc of Cu(II) ions (I_0) was 394.32 mg/L, pH 5.5

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 hrs, 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 goes 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

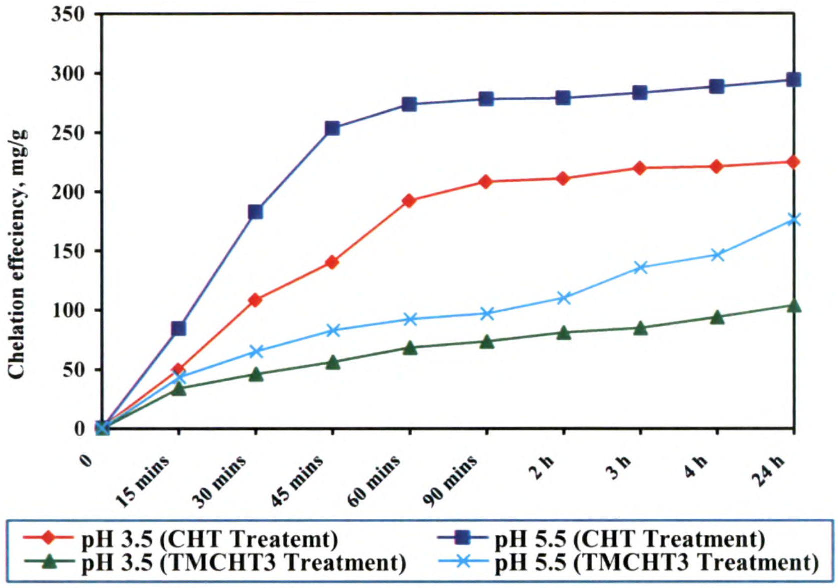
Treatment time	**Residual Cu(II) ions content (I_F, mg/L) in water treated with:**			
	CHT		**TMCHT3**	
	pH= 3.5	**pH= 5.5**	**pH= 3.5**	**pH= 5.5**
15 min	345.35	310.37	360.61	351.07
30 min	286.20	211.79	348.53	329.45
45 min	254.40	141.19	338.35	311.64
60 min	202.25	120.84	326.27	302.10
90 min	186.35	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

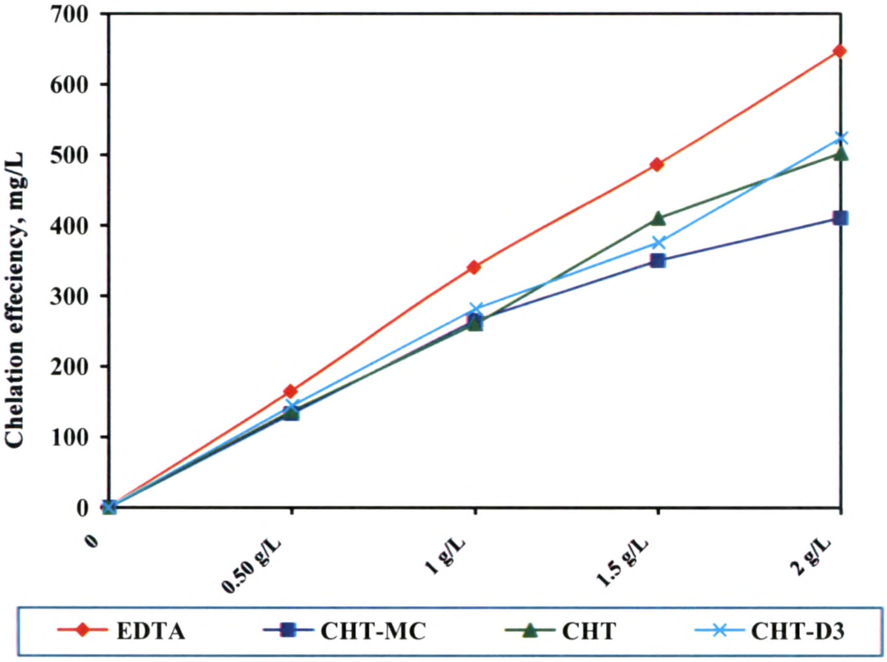
Conc, g/L	Residual Cu(II) content (I_F, mg/L) in water treated with:			
	Na_4EDTA	CHT-MC	CHT	CHT-D3
0.50	593.39	622.01	618.19	610.56
1.00	414.67	489.72	494.81	472.55
1.50	270.30	405.13	344.71	379.69
2.00	108.12	344.71	252.49	230.87

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

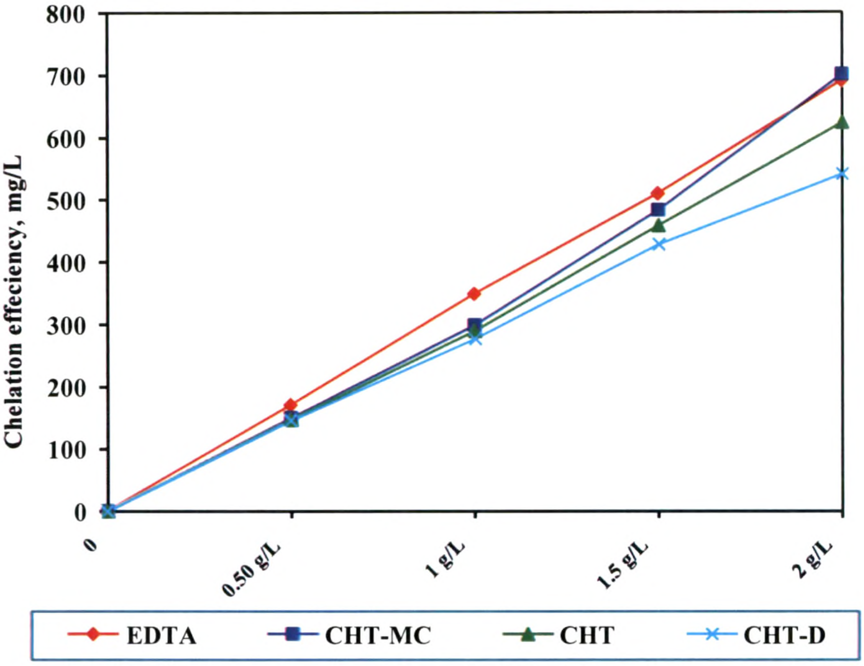
Mol wt of chitosan grades: CHT-MC=654,127, CHT=135,839, CHT-D3=38,733;
Initial conc of Cu(II) ions (I_0) was 754.93mg/L, pH 5.5

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 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

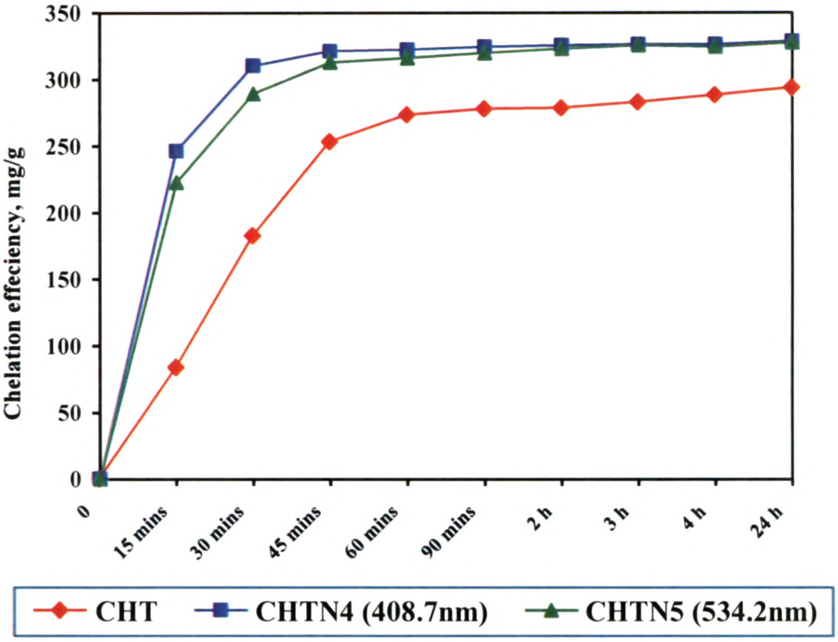
Treatment time	Residual Cu (II) ions content in water (I_F, mg/L) treated with:		
	CHT (Particle size 4014 nm)	**CHTN4 (Particle size 408.73nm)**	**CHTN5 (Particle size 534.2nm)**
15 min	310.37	148.19	171.72
30 min	211.79	83.95	104.94
45 min	141.19	73.14	81.41
60 min	120.84	71.88	78.23
90 min	116.39	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 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 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.

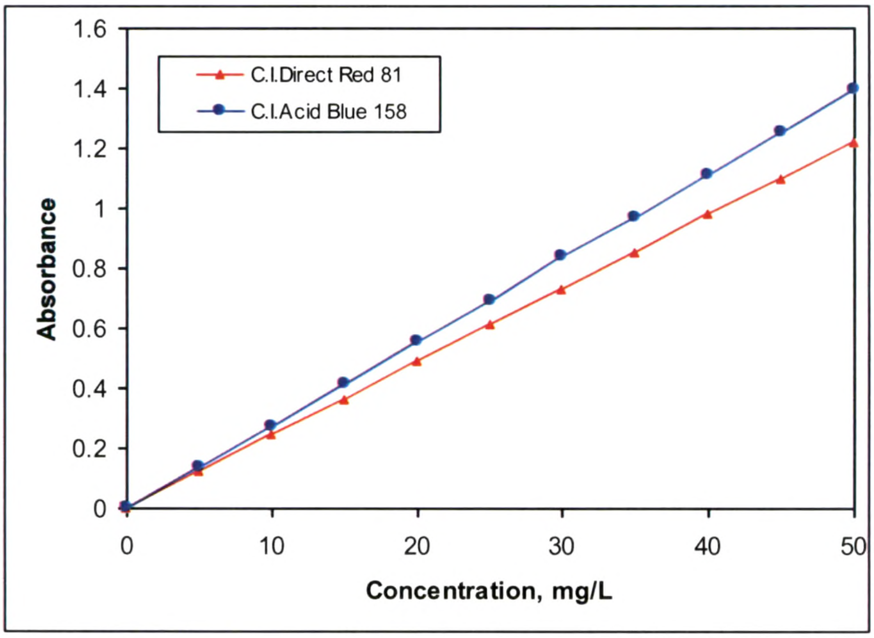


Figure 5.16 Calibration curves for dye solutions

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

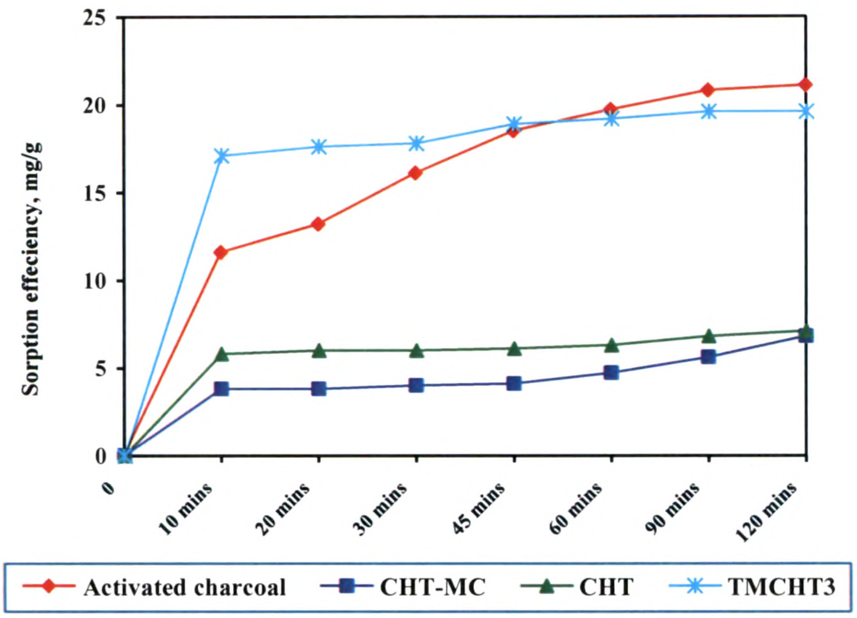
Treatment time, min	**Activated charcoal**		**CHT-MC**		**CHT**		**TMCHT3**	
	O.D.	**Dye content (I_F), mg/L**	**O.D.**	**Dye content (I_F), mg/L**	**O.D.**	**Dye content (I_F), mg/L**	**O.D.**	**Dye content (I_F), mg/L**
10	0.338	13.4	0.516	21.2	0.462	19.2	0.190	7.9
20	0.291	11.8	0.516	21.2	0.460	19.0	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

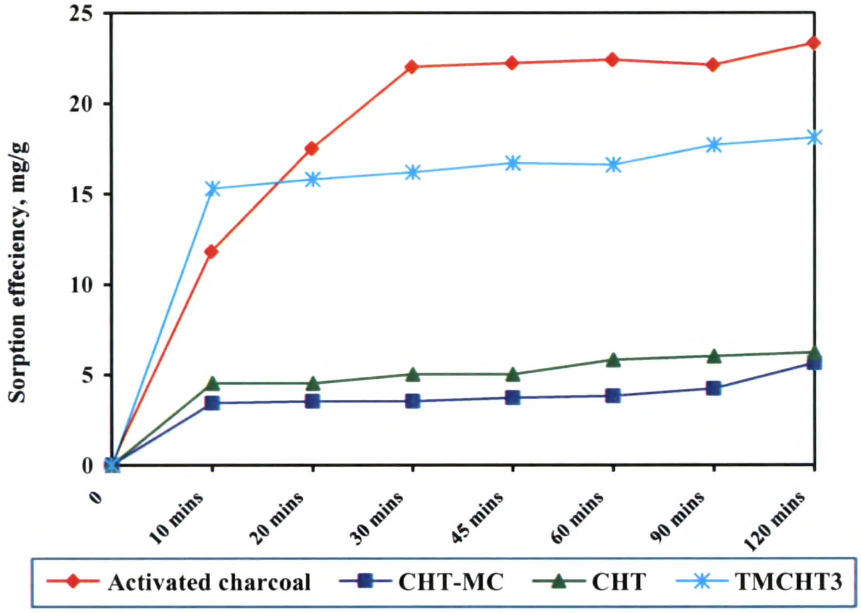
Treatment time, Min	Activated charcoal		CHT-MC		CHT		TMCHT3	
	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L	O.D.	Dye content (I_F), mg/L
10	0.355	13.2	0.595	21.6	0.560	20.5	0.260	9.7
20	0.205	7.5	0.589	21.5	0.560	20.5	0.245	9.2
30	0.070	3.0	0.589	21.5	0.550	20.0	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.Aicd Blue158 at neutral pH

One way to enhance the diffusion of dye into chitosan particles, a pretreatment with swelling 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

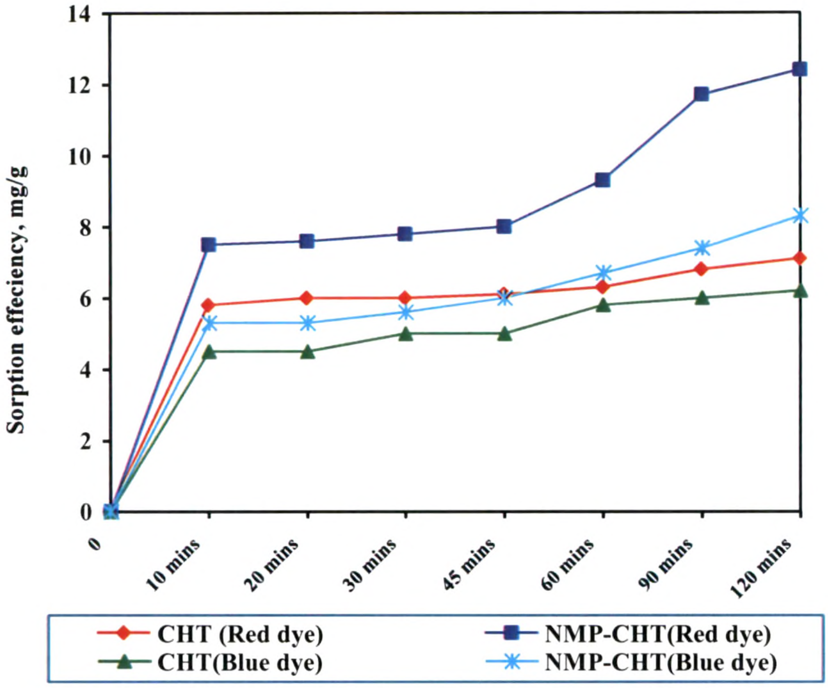
Treatment time, min	**C.I.Direct Red 81**				**C.I.Aicd Blue158**			
	CHT treated effluent		**CHT-NMP treated effluent**		**CHT treated effluent**		**CHT-NMP treated effluent**	
	O.D.	**Dye content (I_F), mg/L**	**O.D.**	**Dye content (I_F), mg/L**	**O.D.**	**Dye content (I_F), mg/L**	**O.D.**	**Dye 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 acid 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

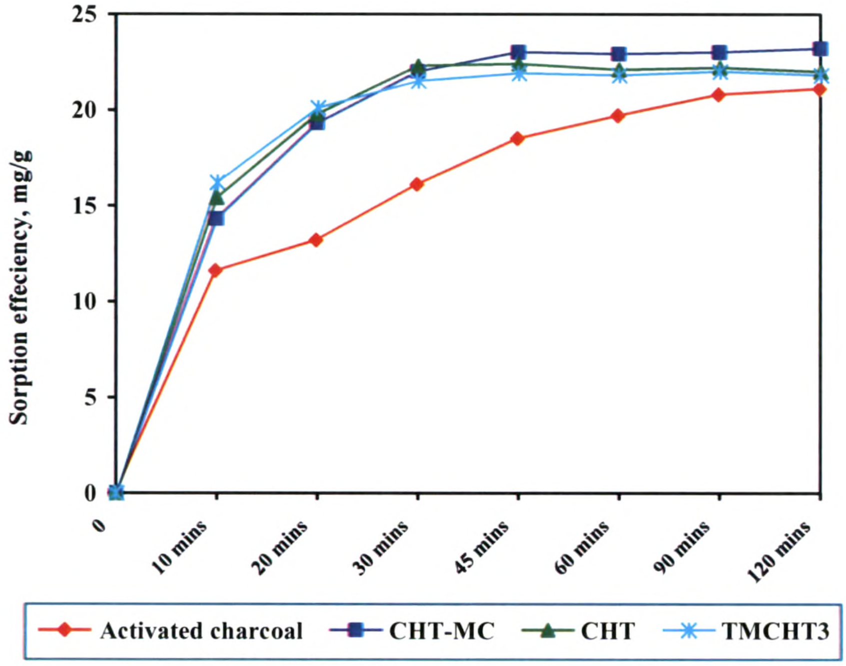


Figure 5.20 Sorption kinetics of C.I.Direct Red 81 at acidic pH

Table 5.37 Residual C. I. Acid Blue158 content in effluent treated with different adsorbents at acidic pH

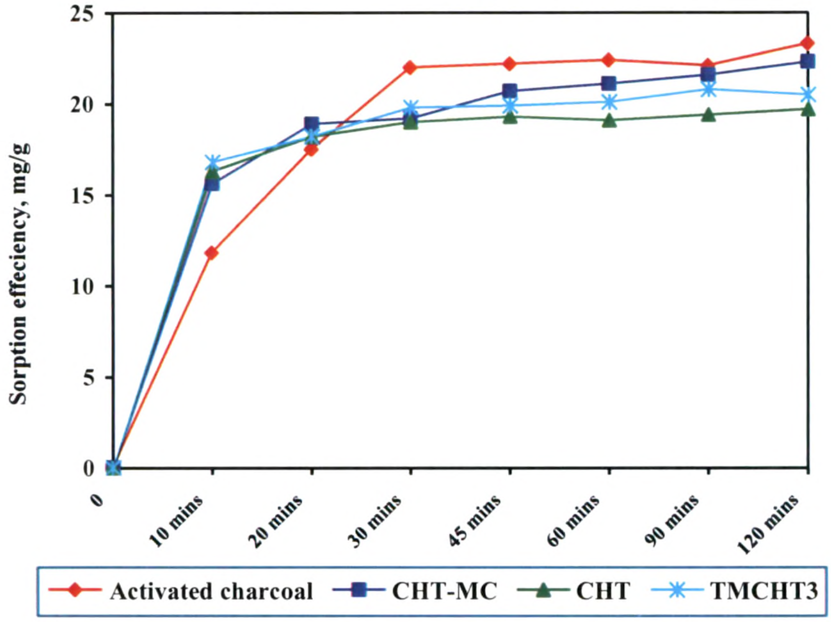
Treatment time, min	Activated charcoal		CHT-MC		CHT		TMCHT3	
	O.D.	**Dye content (I_F), mg/L**	**O.D.**	**Dye content (I_F), mg/L**	**O.D.**	**Dye content (I_F), mg/L**	**O.D.**	**Dye content (I_F), mg/L**
10	0.355	13.2	0.260	9.4	0.230	8.3	0.225	8.2
20	0.205	7.5	0.160	6.1	0.190	6.8	0.190	6.8
30	0.070	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

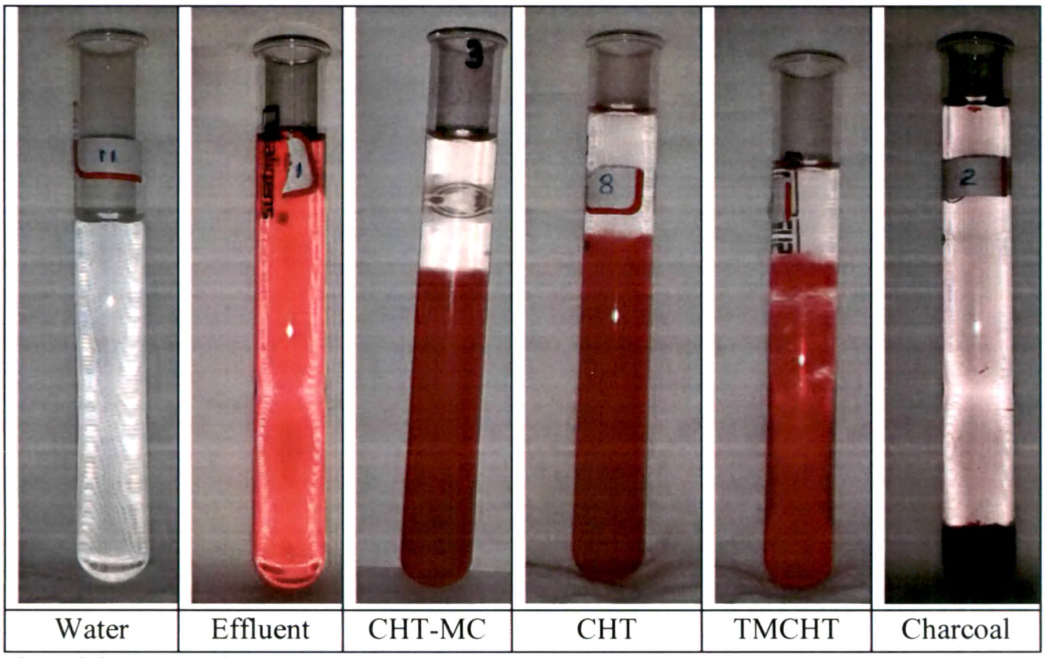
Treatment time, min	Adsorbed C.I. Acid Blue158 (mg/g) from effluent treated with:			
	Activated charcoal	**CHT-MC**	**CHT**	**TMCHT3**
10	11.8 *[47]*	15.6 *[62]*	16.3 *[65]*	16.8 *[67]*
20	17.5 *[70]*	18.9 *[76]*	18.2 *[73]*	18.2 *[73]*
30	22.0 *[80]*	19.2 *[77]*	19.0 *[77]*	19.8 *[79]*
45	22.2 *[89]*	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



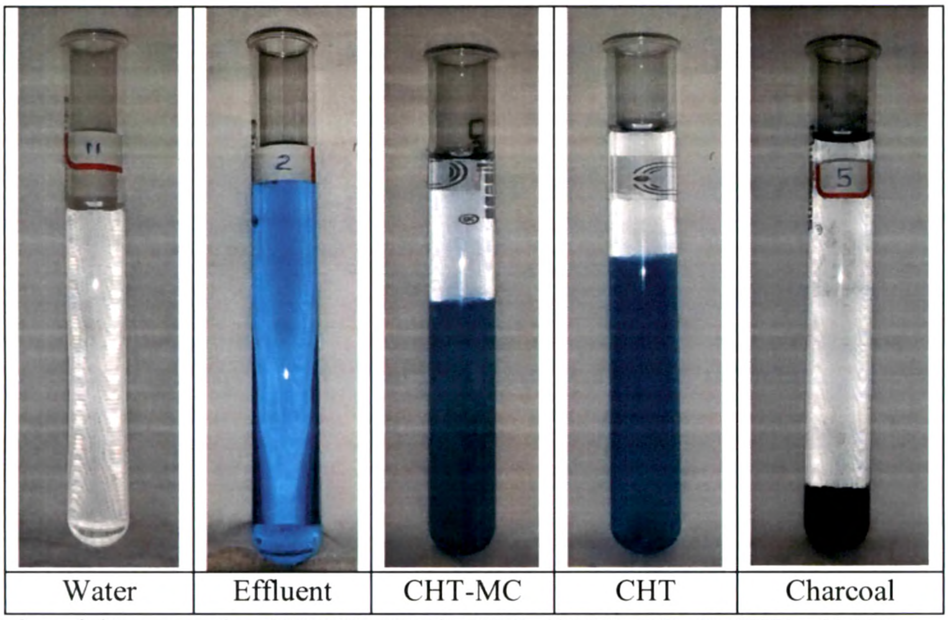
Mol wt of chitosan grades: CHT-MC=654,127; CHT=135,839; DQ: TMCHT3= 50.92%;
Conc of adsorbent 1 g/L, Initial conc of dye (I_0) was 25 mg/L, pH 3.5

Figure 5.21 Sorption kinetics of C.I.Aicd 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



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

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