CHAPTER 6

CONCLUSIONS

Chitosan is a versatile polycationic biopolymer derived from alkaline deacetylation of chitin. Chitosan exhibits several valuable inherent properties such as antibacterial, antifungal, antiviral, antacidity, chelation, non toxicity, biodegradability as well as film formation etc properties. Further, due to its possession of hydroxyl and amino functional groups, chitosan can be fabricated to tailor products with desired functional properties. Keeping in mind these valuable inherent properties and huge application potential, the aim of present study was focused on the applications of chitosan and its various derivatives in textile processing. The work was divided into four major areas:

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

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

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

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

Chapter 2:

Chapter 2 primarily included the studies related to applications of chitosan of varying molecular weights in wet processing of cotton fabric. From the findings of these experiments, following conclusions were drawn.

1. The molecular weights of parent chitosan samples, namely CHT and CHT-MC, were determined viscometrically. These supplied chitosan samples were characterized by FTIR spectroscopy and the structures of both the samples were found identical. Degree of deacetylation (DAC) of chitosan samples was determined by ^{1}NMR spectroscopy and elemental analysis and the values were in close agreement with the data provided by the manufacturer i.e. 90%.

2. Low molecular weight chitosans were synthesized by nitrous acid depolymerization method. The FTIR spectra of chitosan and depolymerized chitosan were almost identical indicating the process of depolymerization caused no chemical change in the structure of the polymer except reduction in molecular weight.
3. The viscosity of chitosan solution was found to be greatly influenced by its molecular weight. The initial molecular weight and the concentration of chitosan were found to influence the stability of its solution. The drop in viscosity in first 24 h was very fast and the critical concentration (C*) point shifted towards right when the storage time was prolonged. The stability of low molecular weight chitosan was not significantly affected within the chosen concentration range. The viscosity of chitosan solution was dropped due to the incorporation of electrolyte (sodium acetate); the effect was more prominent for high molecular weight chitosan solution. Therefore low molecular weight chitosans in presence of suitable electrolyte can be preferably used in textile applications.
4. The SEM of high molecular weight chitosan treated fibres was appeared to be glossy indicating the surface deposition of chitosan, while low molecular weight chitosan treated fibre surface was matty indicating non filmed surface.
5. The stiffness of the fabric was increased due to chitosan treatment which increased with increase in molecular weight and concentration.
6. The absorbency of the fabric was found to be reduced after chitosan treatment, which was deprecated with increase in molecular weight and concentration of chitosan. The drop in absorbency for high molecular weight chitosan treatment may be due to the formation of rigid film of chitosan over the fibre surface.
7. Substantial enhancement in dye uptake of cotton fabric was noticed due to chitosan pretreatment. The dye uptake was increased with increase in concentration and molecular weight of treated chitosan. The extent of improvement was more for the dyes having high molecular weight and containing more number of anionic (sulphonate) groups (e.g. C. I. Direct Blue 71). Almost a salt free dyeing was possible by chitosan pretreatments. But the fastness properties of chitosan pretreated and dyed samples were not satisfactory.

8. A stoichiometric amount of acid dye was taken up by the chitosan treated cotton fabric. Acid dye adsorption test can be employed as a tool for the characterization of chitosan and also the amino groups on cotton fibre.
9. Chitosan treatment did not, however, prove quite suitable for easy care finishing.
10. Chitosan treatment showed improved resistance to rotting in soil burial test. The resistance to microbial attack was due to concerted action of chitosan as polycationic nature, to form a rigid protective coating and as a chelating agent to scavenge the essential metal ions from cytoplasm of microorganism.

Chapter 3:

The very large molecular size and consequently high viscosity of chitosan restricts its penetration into the fibre and fabric structure and leads to only surface deposition. As a result adverse effects on several properties such as appearance, feel and poor fastness properties of dyed samples were observed. Today's need, however, is to improve above properties without altering the inherent natural qualities of cotton. In order to enhance the greater penetration without hampering the useful properties of chitosan, the particle size was reduced to near nano scale by ionotropic gelation technique using TPP as crosslinker. Following conclusions were drawn from the findings of experiments of chapter 3.

11. The particle size and size distribution of the chitosan were analyzed using particle size analyzer.
12. The concentration of chitosan in the formulation bath was found to influence the size of particle. Particle size was reduced with reduction in concentration. Direct preparation method produced particles with comparatively lower size than that found in dilution method.
13. Reduction in molecular weight and in turn drop in intrinsic viscosity decreased the particle size and showed a curvilinear dependence. This relation may be useful in preparation of nano chitosan dispersion of desired particle size.
14. TPP concentration was found to play an important role in controlling the particle size. With increase in concentration of TPP, the particle size was first reduced, reached to minimum and again increased. Excessive TPP led to precipitation.

15. Reduction in particle size reduced the viscosity of chitosan solution significantly, but the storage stability was affected adversely. Use of freshly prepared nano-chitosan dispersions prior to applications may be the remedy.
16. The appearance and handle of nano chitosan treated cotton fabric was much better than the parent chitosan treated one.
17. Nano chitosan treatment showed improvement in fibre strength that increased with the reduction in particle size.
18. Nano chitosan treatment reduced the water absorbency to some extent.
19. The dyeability of both chitosan and nano chitosan treated cotton fabric towards direct dyes was improved reasonably. Acidification of dye bath further improved the dye adsorption and wash fastness of dyed fabric.
20. Nano chitosan together with nano silver treatment showed enhanced resistance to microbial attack.

Chapter 4:

In this chapter synthesis of a series of *N*-substituted chitosan is reported. There were three categories of product viz trimethyl chitosan chloride, *N*-alkyl substituted quaternized chitosan and *N*-aryl substituted quaternized chitosan. From the syntheses and application point of view, following conclusions were drawn.

21. The quaternization of chitosan was characterized by FTIR analysis. The degree of quaternization (DQ) of trimethyl chitosan chloride was determined conductometrically which was in close proximity to that determined by ^{1}HNMR and CHN analysis.
22. DQ of trimethyl chitosan chloride was increased progressively with the increase in concentration of methyl iodide. An optimum amount of alkali (NaOH), co-solvent (NMP) and electrolyte (NaI) was found to be essential to enhance the forward reaction in synthesizing trimethyl chitosan chloride.
23. Different *N*-alkyl chitosan derivatives namely *N*-ethyl, *N*-butyl and *N*-dodecyl; and *N*-aryl chitosan derivatives namely *N*-benzyl and *N*-(1-Naphthyl) methylene chitosan derivative were synthesized by reductive amination of Schiff's base formed by reaction between chitosan and corresponding aldehydes. Characterization was

performed through FTIR for qualitative and conductometry, ^{1}HNMR and CHN analysis for quantitative analysis of *N*-alkyl/aryl *N,N* dimethyl chitosan derivatives.

24. The degree of substitution was dropped with the increase in the chain length of alkyl substituent. Aryl substituents produced lower degree of substitution compared to corresponding alkyl counterpart. The DQ of *N*-alkyl and *N*-aryl chitosan derivatives was decreased with the increase in the molecular size of substituents.
25. The intrinsic viscosity was dropped due to quaternization. Higher the size of the substitution higher was the viscosity. Viscosity of all *N*-substituted quaternized chitosan solutions ware lower in presence of electrolyte. Quaternized chitosan solutions have shown paradoxical behaviour in absence of electrolytes i.e. viscosity increased at high dilutions.
26. *N*-modified chitosan derivatives were applied to cotton fabric by pad-dry cure technique. The appearance of cotton fabric was found to be comparatively improved by it's treatment with quaternized chitosan as against normal chitosan treatment. The feel of the treated fabric was improved with the increase in the chain length of *N*-alkyl substituents. *N*-aryl chitosan derivatives showed moderate improvement in handle.
27. The chlorine retention problem occurred due to chitosan treatment on cotton fabrics was reduced substantially by quaternization of chitosan.
28. The absorbency of trimethyl chitosan chloride treated cotton fabric was improved progressively with the increase in the degree of quaternization. The absorbency of *N*-alkyl/aryl chitosan derivatives treated cotton fabric was dropped.
29. Quaternized chitosan treated fabric showed enhanced dyeability towards direct dye with improved washing fastness properties. The dye uptake was increased with increase in the DQ. It also showed satisfactory dye uptake in absence of electrolyte in the dye bath.
30. Trimethyl chitosan treated cotton fabric showed stoichiometric amount of acid dye adsorption in neutral dye bath.
31. The wrinkle recovery property of cotton fabric was improved to some extent due to *N*-substituted quaternized chitosan derivatives treatment.

32. The chitosan treated samples were soiled more compared with the control one. The quaternization of chitosan was found to improve the soil release properties. The degree of soiling was found to get reduced with the increase in DQ.
33. The quaternization of chitosan was found to improve the resistance towards microbial attack and was improved with increase in the degree of quaternization.

Chapter 5:

Textile wet processing operations produce high volumes of waste water of varying composition that may be harmful to health and environment. It is, therefore, extremely essential that the environmental problems associated with industrial developments are properly addressed for sustainability. As a part of this work, it was found that the presence of excessive amount of calcium in feed water reduced the dye uptake while copper ions reduced the bleaching efficiency of hydrogen peroxide and produced off shades in direct and reactive dyeing. The present investigation (chapter 5) was, therefore, aimed at the understanding the chelation behaviour of chitosan and its derivatives for calcium and copper ions and as a sorbent for removal of traces of dyes from waste water. Chitosan of different molecular weights and quaternized derivatives of varying degree of quaternization were employed in the present experiment. The effect of particle size of chitosan on scavenging efficiency was also examined. From the findings, following conclusions were drawn.

34. The binding of calcium and copper ions to chitosan was confirmed by FTIR. The attachments were mostly effected through coordinate linkages with *O* and *N* of chitosan. The results of iodometric titration method employed for the determination of residual copper ions in water were found to be comparable to that found using atomic absorption spectrometry (AAS). Copper ions adsorbed on chitosan were determined gravimetrically.
35. The chelation behaviour of chitosan derivatives towards calcium and copper ions was found to be almost similar except the extent of sorption capacity which was higher for copper ions.
36. The rate of chelation for metallic ions like calcium and copper was found to be decreased with the increase in the molecular weight of chitosan. The sorption of these

ions was increased with increase in concentration of chitosan. The extent of chelation was found to be high for low molecular weight chitosan when treated for shorter time and decreased with increase in the molecular weight. However very high concentration of chitosan, high molecular weight in particular, is not desirable due to viscosity problems.

37. Highly acidic pH was not found to be suitable for chelation of metal ions. A milder acidic condition (pH 5.5) showed better results.
38. Reduction in particle size of chitosan enhanced both the rate and amount of scavenging of metal ions.
39. The chelation efficiency of trimethyl chitosan was reduced with increase in the degree of quaternization.
40. Chitosan and trimethyl chitosan derivatives were found to be useful adsorbents for colour waste water treatment. Trimethyl chitosan derivative was effective at neutral pH where as normal chitosan required acidic pH. Subsequent mild alkalization could precipitate the chitosan-dye complex and reduce the turbidity.

FUTURE PROSPECTS...

Use of biodegradable and not toxic products from 'natural' sources is growing rapidly and becoming more and more appealing for the replacement of synthetic compounds. Chitosan is a unique polymer that has demonstrated utility in number of applications in textiles. Chitosan, nevertheless, is a versatile product but it requires suitable modifications so that it can be judiciously employed for desired end uses. Therefore, a single product may not necessarily be suitable for all unit operations of textile processing. Therefore suitable structural modifications of chitosans and use of nano technology or combination of both may open a new avenue for its intelligent textile application. In water processing, chitosan may be more suitable for removal of metal ions which may be present in traces i.e. ppm or ppb rather than for industrial or dye house discharge that contains large amount of impurities or else it may used as a sorbent for the isolation of precious metals such as silver, gold or radioactive elements. Introduction of suitable groups or ligands in the backbone of chitosan can enhance its scavenging power and also preference for chelation of specific metal ions.