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Application of chitosan and its derivatives in Cu(II) ions removal from water used in textile wet processing

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Abstract

The applicability of chitosan, trimethyl chitosan chloride and nano chitosan for removal of Cu(II)ions from water used in textile wet processing was studied. The liquor before and after treatment was analysed iodometrically for knowing the presence of Cu(II) ions and FTIR spectroscopy was employed for the characterization of Chitosan-Cu(II) complex. Study included the effect of molecular weight of chitosan, particle size of chitosan and the degree of quaternization of trimethyl chitosan chloride, pH of medium etc on the sorption of Cu (II) ions. The influence of molecular weight of chitosan was found to be an important criteria so far on rate of sorption of Cu(II) ions. Reduction in particle size of chitosan enhanced both the rate and amount of scavenging of metal ions.

Keywords: Chitosan, chelation behaviour, copper ions, nano-chitosan, trimethyl chitosan chloride

Introduction

Plentiful supply of good quality water is indispensable for textile wet processing industry. Water is not only a vehicle to carry or fix the chemicals and dyes, but it is the medium for processing [1]. The water employed for various wet processing operations is now-a-days largely obtained from underground source which is accompanied with various heavy metal ions. The recycled water from effluent discharge also contributes to these impurities due to the inefficiency of conventional effluent treatment plants to remove such traces of metal ions. The presence of these ions, even in ppm level, can have detrimental effects on processes like enzymatic desizing, hydrogen peroxide stability and its bleaching action, shade of dyes etc [2, 3].

Among various metal ions, Cu (II) ion has gained attention due to its both beneficial and as well as adverse effects. Use of copper compounds such as copper sulphate in certain dyeings, direct dyeing in particular, has found to improve the fastness to washing and light. However, presence of copper in water can seriously affect the performance of various unit operations of textile processing such as desizing, scouring, bleaching, dyeing etc. Hence it is advised to avoid copper/brass fittings especially in bleaching plants. Copper is found to be adsorbed by enzyme molecules to form complexes and inactivate the enzymatic action. Copper exhibits a catalytic action on hydrogen peroxide decomposition. Presence of copper is reported to cause instability in peroxide bleaching baths and damage the cotton during bleaching. Copper is readily absorbed on wool and therefore causes damage during peroxide bleaching. Presence of copper ions causes deleterious effect on the shades of various dyes used for cellulose, nylon and protein fibres; nevertheless it enhances the wash and light fastness properties [2, 4].The deleterious effect of Cu(II) ions observed on hydrogen peroxide bleaching of scoured cotton fabric and various direct and reactive dyeing of cotton is presented in Table1 and Figure1. Copper content in textile and allied industries effluent was found to be approximately 77 mg/L [5] as against the WHO norms 0.05 mg/L[5]. Traces of copper (5-45 μg/L) in underground water and about 110 mg/kg of soil in and around Surat (India) have been detected [6].

Table 1 Effect Cu(II) ions on hydrogen peroxide bleaching of cotton fabric

$CuSO_4$ content in	Whiteness	Yellowness	Brightness

bleach bath, mg/L	index	index	index
Control	88.40	1.33	78.08
100	85.98	4.29	73.02
200	85.06	4.69	71.17
500	84.14	5.58	69.32

Scoured sample: *W.I. = 78.07, Y.I. = 17.02 and B.I. =56.91*

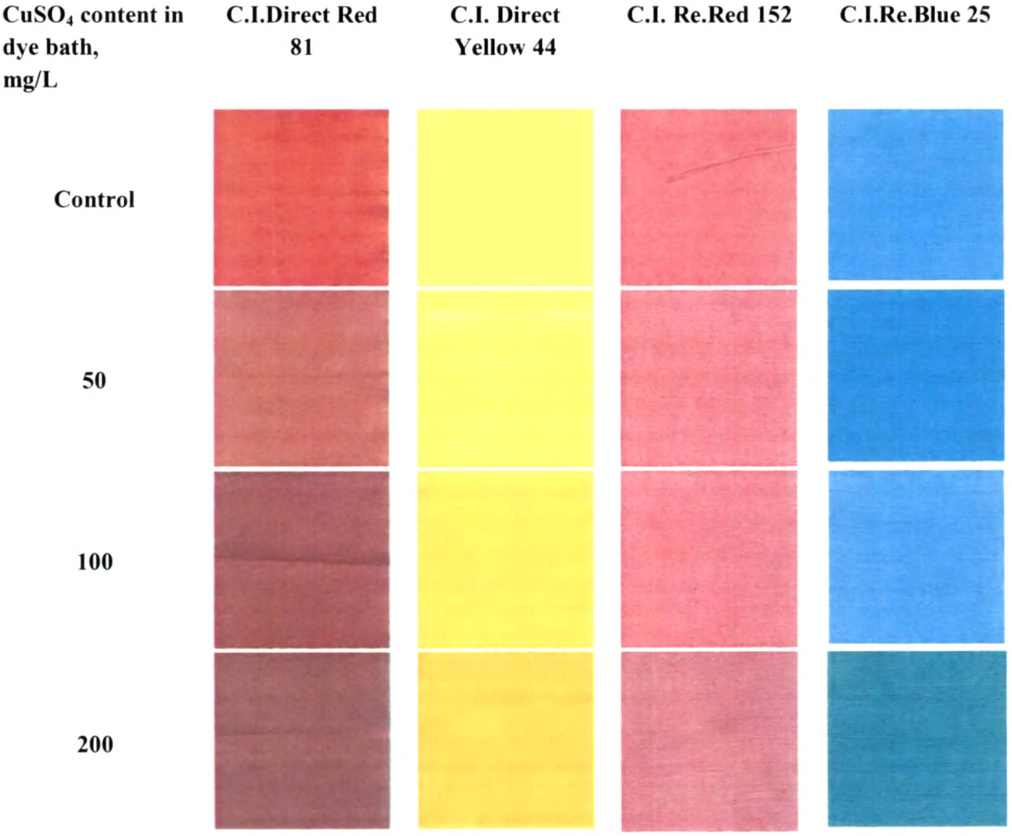


Figure 1 Effect of Cu (II) ions in dye bath on the shades of direct and reactive dyeing on cotton fabric

The adverse effect of such metal ions can be controlled either by using chelating agents like ethylene diamine tetra acetic acid (EDTA), diethylene triamine penta acetic acid (DTPA), nitrilo triacetic acid (NTA) etc [7] or metal ions can be chemically precipitated or coagulated as salts or reduced to metallic form. They can be separated out from the liquid phase by filtration, settling, centrifuging or electro deposition [1,8,9]. Various natural products such as wood bark and clay [10], rice hull, cotton fibres, bamboo pulp, peanut skin etc and chitosan have been found to remove metal cations from the streams [11-14]. The detrimental effects on environment still persist when water is treated through first route due to the existence of metal ions in discharged water, while metal ions are removed from discharged water by second route is safer.

Chitosan is a natural based product derived from alkaline deacetylation of a biopolymer, chitin. It is second most abundant biopolymer after cellulose. The amount of presence of primary amino groups present on chitosan molecule is characterized by degree of deacetylation (DAC) [15]. The application potential of chitosan and its derivatives for the recovery of valuable metals or the treatment of contaminated effluents is well documented [16, 17]. Our earlier report [18] has shown the scavenging property of chitosan for calcium ions. Karthikeyan et al. [19] studied the dynamics and equilibrium sorption of Zn (II) on to chitosan. They observed maximum of six minutes were required for complete sorption of Zn ions by chitosan obeying the Freundlich and Langmuir isotherms. Nomanbhay and Palanisamy [20] used chitosan coated oil palm shell charcoal successfully for the adsorption of chromium ions from water. Bioconversion of highly toxic Cr(VI) into Cr(III) was also observed, which is essential in human nutrition especially in glucose metabolism. Chang and Chen [21] isolated Au (III) ions from water on chitosan coated Fe_3O_4 nanoparticles. They found that the gold ions could be fast and efficiently adsorbed. E.Guibal et al.[22] synthesized thiourea derivative of chitosan for platinum and mercury recovery owing to the chelating affinity of sulphur ligands. Abdel Mohdy et al. [23] introduced diethyl amino ethyl methacrylate (DEAEMA) groups onto chitosan backbone through radiation grafting and studied the chelation property of grafted derivative on copper, zinc and cobalt ions. They reported that the extent metal ions uptake by chitosan-DEAEMA derivative was preferentially higher for copper ions followed by zinc and cobalt ions. The present investigation was aimed at understanding the chelation property of chitosan and its derivatives towards Cu(II) ions. Chitosan of different molecular weight, nano chitosan of varying particle size and trimethyl chitosan derivative of different degree of quaternization were taken for the study. The test sample before and after treatment was analysed iodometrically for knowing the presence of Cu(II) ions and FTIR spectroscopy was employed for the characterization of Chitosan-Cu(II) complex.

Materials and Methods

Materials: 100% cotton fabric (warp and weft 40s, ends/inch142, picks/inch 72 and g/m^2 125), at ready for dyeing stage, was procured from Mafatlal Industries Ltd, Nadiad, Gujarat State,India. Chitosan of different molecular weights were obtained from Marine Chemicals, Kerala State, India (CHT-MC) and Mahtani Chitosan Pvt. Ltd., Gujarat State, India (CHT). A low molecular weight chitosan (CHT-D) was synthesized from CHT by depolymerization with nitrous acid as described earlier [25]. The specifications of different grades of chitosan are given in Table 2. Various direct and reactive dyes namely C.I.Direct Red 81, C.I. Direct Yellow 44, C.I. Reactive Red 152 and C.I. Reactive Blue 25 were kindly supplied by Colourtex Industries Ltd, Gujarat State, India. Anionic detergent (Ezee, Godrej, India) employed was of commercial grade.

Other reagents like Acetic acid, Acetone, Methyl alcohol, Methyl Iodide, EDTA, Sodium thiosulphate, Potassium iodide, Sodium iodide, Sodium hydroxide, Soda Ash, Sodium sulphate, Copper sulphate, N-methyl-2-pyrrolidone (NMP) etc used were of analytical grade.

Synthesis of trimethyl chitosan chloride

Trimethyl chitosan chloride (TMCHT) was synthesized as follows: purified chitosan (CHT) (1g) was treated with required amount methyl iodide (5 g and 15g for two different levels of degree of quaternization) in presence of sodium iodide 2.4g and sodium hydroxide (2g) dispersed in N-methyl-2-pyrrolidone (NMP)(40 mL) in a stainless steel reaction vessel at 50^{0}C for 24h. Trimethyl chitosan iodide was recovered from using acetone then subjected to ion exchange by treatment with sodium chloride (10%, 50 mL) for 1h. TMCHT was then recovered from acetone with repeated washings and oven dried at 55^{0}C.

Synthesis of Nano chitosan dispersions

The method for synthesis of nano chitosan dispersions was followed same as discussed elsewhere [18]. The prepared nano-chitosan (CHTN) from the starting material CHT was stored in refrigerator. The particle size and size distribution of the chitosan were analyzed on the particle size analyzer (Zetasizer Nano ZS90, Malvern Instruments Ltd, UK).

Hydrogen peroxide bleaching of cotton fabric

Scoured cotton fabric was treated with solution containing hydrogen peroxide (30%, 10 g/L), soda ash (10 g/L) sodium silicate (10 g/L), and detergent (1 g/L) at about 85 ^{0}C for 60 minutes. The material- to- liquor ratio was maintained at 1:30. After bleaching was over, the fabric was washed at 80 ^{0}C for 20 minutes and then rinsed.

Dyeing with Direct Dyes

The cotton fabric was dyed with direct dye (1% o.w.m.) in presence of Glauber's salt (20% o.w.m.) and soda ash (5% o.w.m.) at temperature 90 ^{0}C for 60 minutes. The material- to- liquor ratio was maintained at 1:40. The dyed sample was then rinsed with cold water 3 times, air dried and hot pressed. The dyed samples were evaluated for colour strength in terms of K/S values on computer colour matching system (Spectroscan 5100A, Premier Colorscan, India).

FTIR Analysis

FTIR of CHT and TMCHT derivatives were taken on a Thermo Nicolet iS10 Smart ITR spectrophotometer (Thermo Fisher Scientific, USA) in the wavenumber between 4000–500 cm^{-1}.

Treatment of Cu(II) ions containing water with chitosan derivatives

Required quantity of chitosan or chitosan derivative (e.g.1g/L) was treated with copper sulphate solution corresponding to Cu(II) ions concentration of 394.32 mg/L in presence of acetic acid (0.7 mL/L for pH 5.5 and 1.5 mL/L for pH 3.5) with occasional stirring. After the prescribed reaction time is over, chitosan was precipitated out by the addition of few drops of sodium hydroxide (10%) solution. The solution was then filtered, the filtrate was analysed for Cu(II) ions content iodometrically and the residue was analysed for FTIR spectroscopy.

Iodometric method for determination of Cu(II) ions

100 mL aliquot (sample solution) was taken in a conical flask and mixed with 10 mL of 10% liquor ammonia to obtain a dark blue colour. The solution was then neutralized with acetic acid; a slight excess acid was added, followed by 2 g of potassium iodide. The flask was placed in dark for about 15 minutes for complete liberation of free iodine and then titrated against 0.1N sodium thiosulphate using starch as indicator. Ammonium thiocyanate (2 g in 10 mL water) was then added and titration continued. The amount of Cu(II) present in the given solution was calculated following equation [25].

$$\text{Cu(II) ions content, mg/L} = \frac{A \times 6.36 \times 1000}{V}$$

Where, 'A' is the amount (mL) of 0.1N $Na_2S_2O_3$ taken in burrette and 'V' is thevolume (mL) of aliquot taken for titration (100 mL)

$$\text{Chelation efficiency in terms of sorption of Cu(II) ions by chitosan (mg/g)} = \frac{I_0 - I_F}{M}$$

$$\text{Chelation efficiency in terms of copper ions removal from water (mg/L)} = I_0 - I_F$$

Where, I_0 is the initial concentration (mg/L) of Cu(II) ions and I_F is the concentration(mg/L) of Cu(II) ions in treated water. M is the mass (g) of chitosan.

Results and Discussion

Characterization and mechanism of chelation of copper (II) ions on chitosan

The important ligands on chitosan macromolecule that form complex with metal ions are oxygen pertaining to primary and secondary hydroxyl groups and nitrogen belonging to amino and acetamido groups. The structural changes in chitosan occurred due to chelation with Cu(II) ions can be conveniently studied using FTIR spectra analysis. The FTIR spectra of CHT and CHT-Cu complex are presented in Figure 2 and Figure 3.

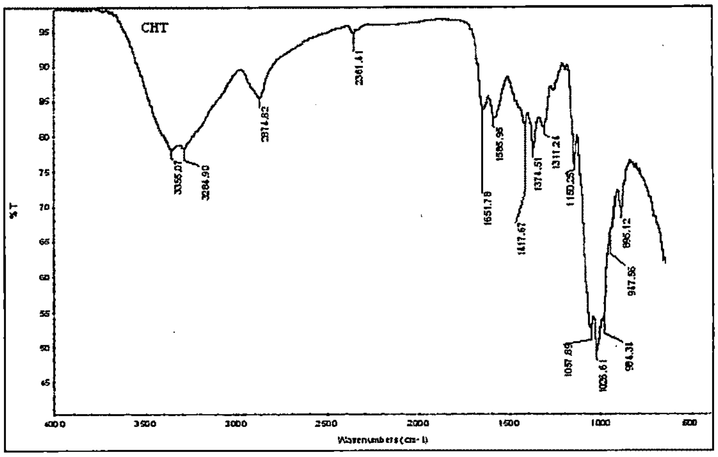


Figure 2 FTIR spectrum of CHT

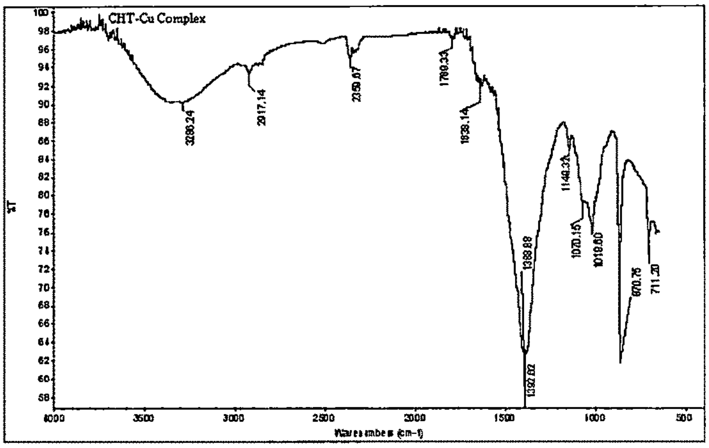


Figure 3 FTIR spectrum of CHT-Cu complex residue

The broad bands at wave numbers 3355, 3284cm^{-1} of the FTIR spectrum of chitosan (Figure 2) may be attributed to O-H, NH and NH_2 stretching. The absorption band at 1651 cm^{-1} was due to C=O (carbonyl) stretching of secondary (amide I) amide bond, a characteristic of N-acetyl group and the medium peak at 1585 cm^{-1} appeared due to bending vibrations of N-H of amide II bond (N-acetyl residue) and the primary amine. Another medium absorption peak at 1374 cm^{-1} was attributed to the N-H linkage of amide III. A strong absorption peak at 1025 cm^{-1} was due to primary hydroxyl group, characteristic peak of -CH_2OH in primary alcohols, arised from C-H stretching [26, 27]. The structural changes in chitosan arised due to complex formation with copper ions were observed in the spectrum as shown in Figure 3. The broadening of the peak at 3355 cm^{-1} and progressive reduction of peak at wave number at 1025cm^{-1} indicated the involvements of amino and hydroxyl groups in the scavenging of the Cu(II) ions. Formation of a new peak at 1392 cm^{-1} and modifications in peaks due to various amide groups characterized interaction of these groups with Cu(II) ions [28]. The complex formation of chitosan with copper ions may be explained with the help of its electronic configuration of copper ions. Copper, though not strictly termed as transition metals as their *d* orbitals are complete, still they form a number of complexes when their ions have incomplete *d* orbitals e.g. in the case of Cu(II) ions having the coordination numbers usually 2,4,and 6 facilitate coordinate bond formation [29]. The possible ways of Cu(II) ions bound to chitosan is illustrated in Figure 4.

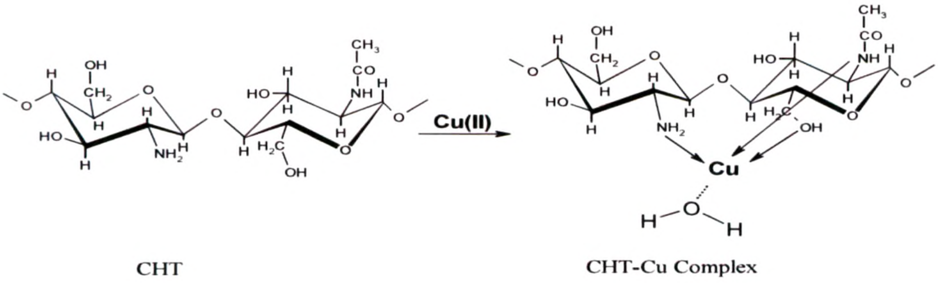


Figure 4 Chelation of Cu (II) ions by chitosan

In order to understand the chelation property, chitosans in various forms and grades were employed as listed in Table 2 and the performance were compared with tetra sodium salt of ethylene diamine tetra acetic acid (Na_4EDTA).

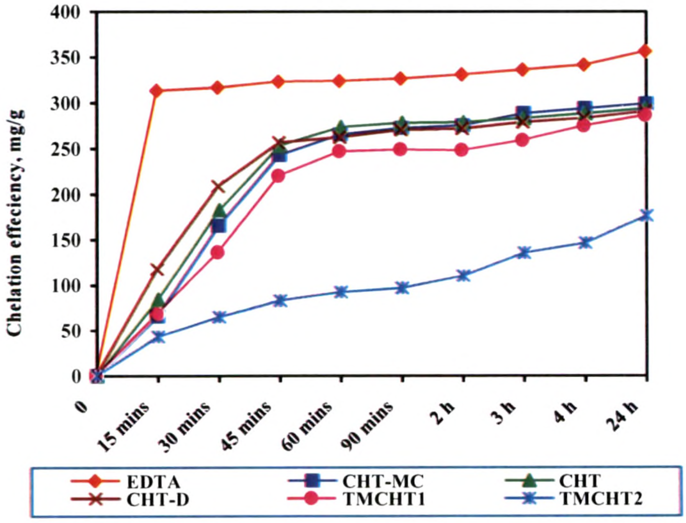
Table 2 Chitosan derivatives employed for chelation study

Sample code	Chemical Name	Properties			
		DAC, %	Molecular weight	Particle size nm	DQ, %
CHT-MC	Chitosan	89.03	654,127	-	-
CHT	Chitosan	90	135,839	4014	-
CHT-D	Chitosan	90	38,733	-	-
CHTN1	Nano-chitosan	-	-	408.73	-
CHTN2	Nano-chitosan	-	-	534.2	-
TMCHT1	Trimethyl chitosan chloride	-	-	-	13.41
TMCHT2	Trimethyl chitosan chloride	-	-	-	50.92

DAC: Degree of deacetylation, DQ: Degree of quaternization

Effect of structural modification of chitosan on chelation of Cu (II) ions

The extent of copper ions binding of chitosan is believed to be dependant on the availability of number of electron donating ligands such as O and N. The state of these ligands on chitosan macromolecules is anticipated to be altered due to chemical modifications such as quaternization. The Cu(II) ions sorption by various chitosan derivatives at pH 5.5 is shown graphically in Figure 5.



Concentration of chelating agent 1g/L, Initial concentration of Cu(II) ions 394.32 mg/L, pH 5.5
Figure 5 Chelation behaviour of chitosan derivatives for Cu(II) ions

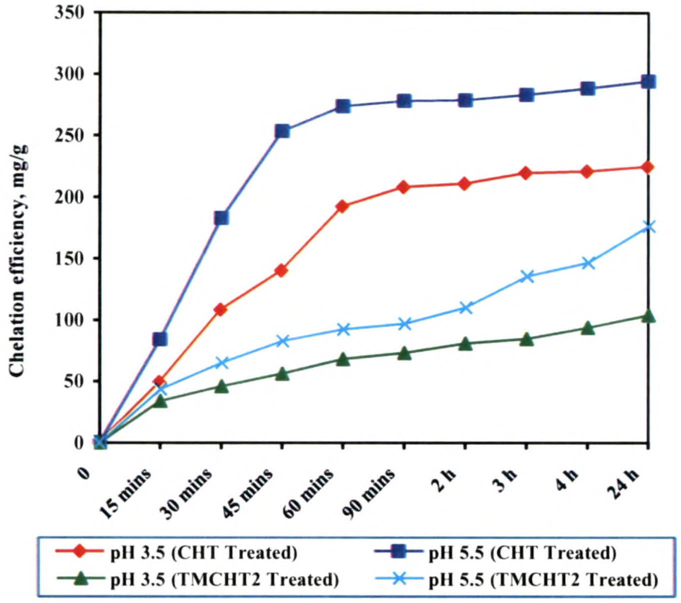
Figure 5 illustrates that EDTA attained the equilibrium rapidly for the copper ions binding and the chelation capacity was maximum. The prolong treatment showed little improvement in chelation efficiency after initial 15 minutes treatment. The chelation behaviour of chitosan was comparatively slower. The molecular weight of chitosan was found to have a little effect on its chelation behaviour. At the onset and during the first hour of treatment, the rate of chelation was slightly higher for low molecular weight chitosan. When the treatment was continued for longer time the copper ion sorption was levelled off for different molecular weight chitosans. With increase in molecular weight of chitosan (CHT-MC), the rate of sorption of copper ions was slowed down but the absolute adsorption after prolong treatment (>3h) was higher. Thus, the influence of molecular weight of chitosan, in first hour of treatment, seemed to be more pronounced on the rate of sorption rather than on absolute sorption of copper ions. Modification of chitosan by quaternization process was found to reduce its metal binding capacity. The chelation capability of trimethyl chitosan (TMCHT) was decreased with increase in degree of quaternization.

A substantially higher chelation power of EDTA may be attributed to the combined effect of ionic linkages of Cu(II) cations with anionic carboxylate groups and the coordinate bonds with amino groups. The electrostatic attraction between EDTA and metal cations may be the driving force for the attachments. Chitosan, on the other hand, is a polymeric material having rigid conformation. When dissolved in water in presence of acid, most of the amino groups are protonated and therefore are incapable of bonding with copper cations. The only possible route of interaction is through unprotonated amino groups, hydroxyl groups and/or N-acetyl groups. Further, these polycationic macromolecules in solutions are mostly swollen entangled bunches exposing very small surface area and hence provide less ligands for interaction with metal ions. The chitosan molecules, therefore, are slower in chelation compared with EDTA. The latter inactivates metal ions but does not remove them. On the other hand, Chitosan, a biodegradable chelating agent, removes metal ions even when present in traces. The process can be made faster by using nano chitosans, chemical modifications of parent chitosan etc. It is a better choice for medical usage. Being polycationic polymeric material, chitosan can easily undergo sedimentation due to nucleation and can be removed simply by decantation or by sand filtration. On account to this unique property, chitosan can be used to minimize the turbidity in water treatment. Since the treatment is done prior to final filtration, no additional filtration is required.

The availability of accessible interactive ligands for chelation is determined by the physical state of macromolecules in solvent which in turn is determined by its molecular size and hence the molecular weight. Low molecular weight chitosans (CHT-D) in solution are comparatively more extended and mobile due to less intra and intermolecular forces and thus provide more surface area for chelation reactions and therefore shows enhanced rate of sorption. Conversely, high molecular weight chitosan (CHT-MC) molecules in solution are more entangled and compact with lesser accessibility of ligands which led to lower rate of sorption of Cu(II) ions. On prolong treatment, large sized chitosan molecules slowly under goes depolymerization due to hydrolysis, which results in fall in viscosity as was observed earlier[18] leading to opening of sites and continued chelation. The chelation property of trimethyl chitosan chloride (TMCHT), however, was reduced as some of the amino groups were engaged in forming bonds with methyl groups which consume the lone pair of electrons of nitrogen and also the presence of bulkier methyl groups restricts the diffusion of metal ions. For unmodified chitosans, recycling of the used product would be difficult as the attachment of metal ions to chitosan is accomplished by the coordinate linkages. But chemical modification of chitosan by introducing anionic groups like carboxyl, sulphonate etc can impart ion exchange property. The treatment of chitosan is effective in removing traces of metal ions and hence can be beneficial in isolation of precious metals

Effect of pH on chelation of Cu (II) ions

An important parameter that alters the state of ligands on chitosan and its derivatives is the pH of medium. Acidic pH is required for dissolution of chitosan in aqueous medium; however, it leads to protonation of amino groups. In order to understand the effect of pH on chelation behaviour of CHT and its quaternized derivative of maximum degree of quaternization i.e.TMCHT2, two different pH were selected namely pH 3.5 and pH 5.5. Higher pH (pH ~7) was avoided due to the formation of hydroxides of copper causing precipitation [30]. The sorption of Cu(II) ions by CHT and TMCHT2 as a function of pH is presented in Figure 6. CHT was found to be more efficient in complex formation with Cu(II) ions at pH 5.5. Similar results were observed in case of TMCHT2 though found to be less efficient compared with CHT. It is known that the attachment of Cu(II) ions with chitosan is possible through co-ordinate bonds by the donation of lone pair of electrons of amino, acetamido and hydroxyl groups. In highly acidic medium i.e. at pH 3.5 most of the amino groups are protonated and therefore they do not remain available for coordinate bond formation. In that case the scavenging of Cu(II) ions would be assigned to hydroxyl and N-acetyl groups. At slightly higher pH (pH 5.5), some of amino groups remain unprotonated or free. The free amino groups, due to the presence of lone pair of electrons, are capable of forming coordinate linkages with copper ions and hence an improvement in chelation was observed at pH 5.5. TMCHT exerts ionic repulsion to copper cations and in addition the bulkier side methyl groups act as a barrier and leads to the reduction in chelation efficacy of trimethyl chitosan.

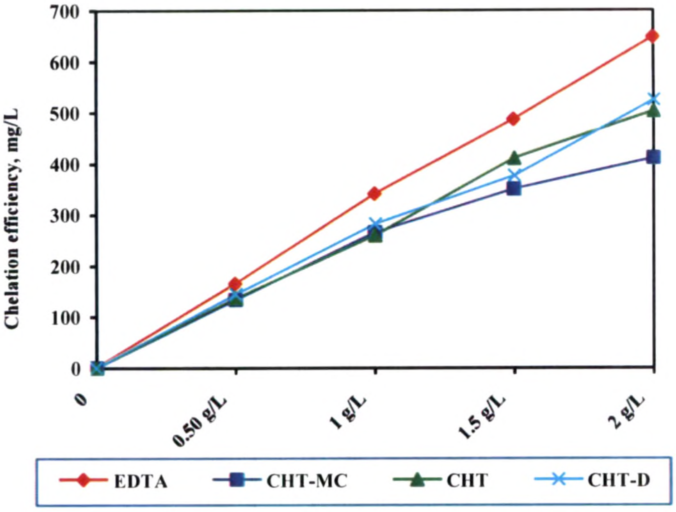


Concentration of chelating agent 1g/L, Initial concentration of Cu(II) ions 394.32 mg/L

Figure 6 Effect of pH of the medium on the chelation behaviour of chitosan derivatives at different time intervals

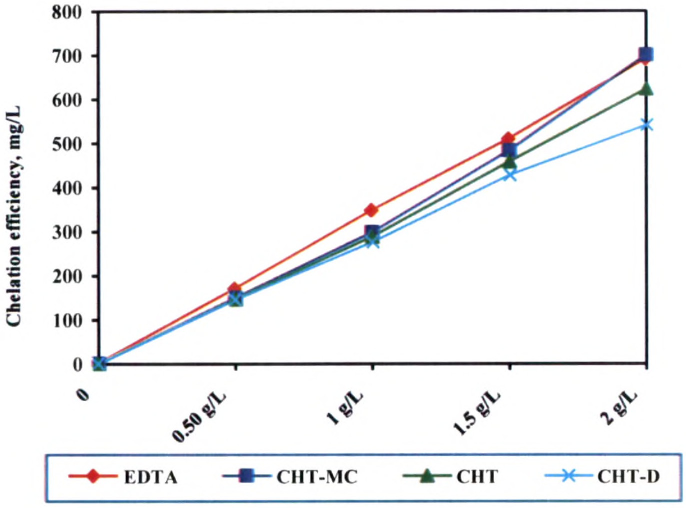
Effect of concentration of chitosan derivatives on chelation of Cu(II) ions

An important parameter that influences the sorption of metal ions is the concentration of chelating agent. The aqueous behaviour of chitosan was found to be governed by the storage time and the behaviour of chitosan in solution may affect the chelation capacity [20]. Thus, in order to understand the chelation behaviour, the effect of different concentration and molecular weights of chitosan on the removal of copper ions from water for two different durations of treatment, namely, short (1h) and long (24h) treatment time respectively was studied. The results are shown in Figure 7 and Figure 8.



Initial concentration of Cu(II) 754.93mg/L, pH 5.5

Figure7 Effect of concentration and molecular weight of chitosan on chelation efficiency for 1h treatment



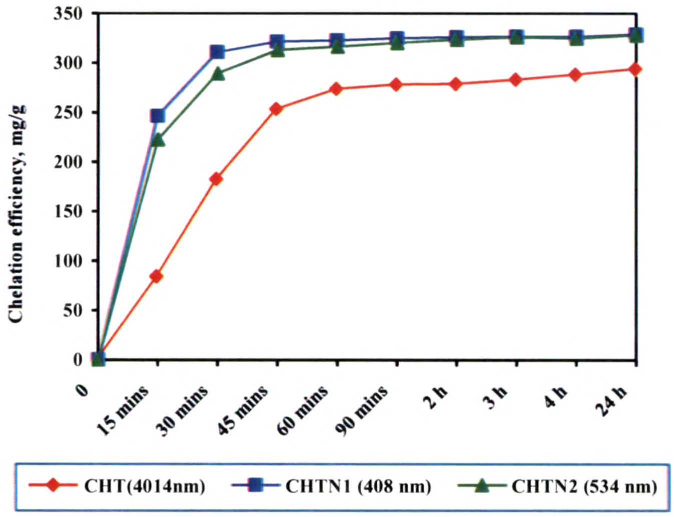
Initial concentration of Cu(II) 754.93mg/L, pH 5.5

Figure 8 Effect of concentration and molecular weight of chitosan on chelation efficiency for 24h treatment

It is observed from Figure7 and Figure 8 that the sorption curves for EDTA followed linearity with respect to concentration and almost same level of chelation efficacy observed for both the durations of treatment. The amount of Cu(II) ions removed from treated liquor was found to be increased with increase in concentration of chitosan derivatives. The sorption curve for low molecular weight chitosan (CHT-D), when treated for short time (1h), was found to be linear within chosen concentration range while high molecular weight chitosans showed some deviations at higher concentrations (Figure 7).The chelation efficiency of different forms of chitosan was found to follow the following trend CHT-D>CHT>CHT-MC. On prolong treatment i.e. when the treatment was extended to 24 h (Figure 8), the chelation behaviour of chitosan was altered particularly for high molecular weight chitosans. The chelation behaviour of low molecular weight chitosan (CHT-D) was not much influenced. The chelation efficiency of chitosans was, however, reversed as against short duration of treatment i.e. CHT-MC>CHT>CHT-D. The linearity observed for low molecular weight chitosan (CHT-D) can be ascribed to the presence of their molecules in solutions in comparatively free and more extended form due to less intra and intermolecular forces. These molecules provide, in chosen concentration range, uniform number of sites proportional to the concentration of chitosan. During short treatment time, high molecular weight chitosan (e.g. CHT-MC) molecules in solution still remain entangled due to overlapping of macromolecules as revealed by the viscosity measurement reported elsewhere [18]. Therefore they provide fewer sites for the interaction with Cu(II) ions resulting in to decreased chelation. On prolong treatment, high molecular weight chitosans may undergo depolymerization due to hydrolysis and may also display more opened conformation due to disentanglement leading to opening up of more sites for chelation, which is more prominent at higher concentration [30,31]. Thus it is the depolymerization leading to opening up of molecular conformation comparatively more prominently in high molecular weight chitosan than in low molecular weight chitosan on prolong treatment and what we virtually see is the reversal in chelation efficiency on prolong treatment.

Effect of particle size of chitosan on chelation of Cu(II) ions

The reduction in particle size of chitosan macromolecule to nano level can furnish increased surface area and hence more number of reactive sites (ligands) for metal scavenging. The particle size of chitosan was reduced by ionotropic gelation with sodium tripolyphosphate (TPP) as described earlier [32]. The varying levels of particle size of nano chitosan, for a given molecular weight chitosan, were obtained by varying the concentration of chitosan. Two different nano chitosans of average particle sizes 408 nm and 534 nm were obtained from CHT from initial concentrations of 1.5 g/L and 2 g/L. These stocks solutions were employed for chelation study of copper ions at concentration 1g/L, obtained by dilution. The effect of particle size on the chelation efficiency of chitosan is shown graphically in Figure 9. The results revealed that the rate of chelation enhanced by the reduction in particle size of chitosan indicating faster establishment of equilibrium with higher equilibrium chelation efficiency. Besides the increased surface area due reduction in particle size, the presence of TPP can also act as a ligands for scavenging the copper ions [29].



Concentration of chelating agent 1g/L, Initial concentration of Cu(II) ions 394.32 mg/L, pH 5.5

Figure 9 Effect of particle size on chelation efficiency of CHT for Cu(II) ions

Conclusion

The presence of excessive copper ions adversely affect the bleaching efficiency and dyeing results. Chitosan of different molecular weights and quaternized derivatives of varying degree of quaternization were employed in the present experiment. The effect of particle size of chitosan on scavenging efficiency was also studied.

The binding of copper ions to chitosan was confirmed by FTIR. The chelation efficiency of trimethyl chitosan (TMCHT) was reduced with increase in the degree of quaternization. Highly acidic pH was not found to be suitable for chelation of metal ions. A milder acidic condition (pH 5.5) showed better results. The sorption of copper ions was increased with increase in the concentration of chitosan/chitosan derivatives. The extent of chelation was found to be high for low molecular weight chitosan when treated for shorter time and decreased with increase in the molecular weight whereas for higher sorption time a reverse trend was noticed. Reduction in particle size of chitosan enhanced both the rate and amount of scavenging metal ions.

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Improvement in properties of cotton fabric through synthesized nano-chitosan application

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In this paper, the study on synthesis, characterization and application of nano-chitosan on cotton fabric has been reported. The nano-chitosan treated fabrics are then tested for appearance, tensile, absorbency, stiffness, dyeing behaviour, wrinkle recovery and antibacterial properties. Low molecular weight chitosans are prepared by nitrous acid hydrolysis method; the molecular weights are determined viscometrically. Nano-chitosans are synthesized by ionic gelation of pentasodium tripolyphosphate and chitosan, and then characterized by particle size determination. The fabric samples are pretreated with normal and nano-chitosan solutions by pad-dry-cure technique. The surface morphology of treated cotton fabric has been studied by SEM analysis. The treated fabrics have also been dyed and their whiteness, yellowness and brightness indices are evaluated. It is found that the particle size and polydispersity of chitosan in solution are affected by the variation in molecular weight. The dye uptake and wash fastness of nano-chitosan treated fabrics are found to be improved. An enhanced antibacterial property is observed with the reduction of nano-chitosan particles and when coupled with nano silver colloid.

Keywords: Antibacterial property, Chitosan, Cotton, Dyeing behaviour, Nano-chitosan, Wrinkle recovery

1 Introduction

Various wet processing operations of textiles from initial preparatory processes to final finished clothes are now focused for green technology. Several conventional non-ecofriendly chemicals are being replaced by natural based products that are safe to environment and health during manufacturing and usage. Applications of enzymes in preparatory and in bio-polishing, natural dyes for coloration, biopolymers and their derivatives in fibre production and finishing processes, etc are some of them. One such biopolymer of great interest in recent years is chitosan, derived from alkaline deacetylation of chitin[1].

The precursor chitin is a nitrogen containing polysaccharide, which is second most abundant biopolymer after cellulose; distributed in the shells of crustaceans such as crabs, shrimps and lobsters as well as in the exoskeleton of marine zoo-plankton, including coral, jellyfish and squid pens. It is totally ecofriendly and renewable[2,3].

Chemically, chitosan is a linear (1–4) linked 2- amino-2-deoxy-β- d- glucan (i.e. β- d-glucosamine) having the structure very much close to that of cellulose except the hydroxyl group in C (2) of cellulose is being replaced by amino group in chitosan. Indeed, it is a copolymer of N-acetyl-glucosamine and glucosamine units. Being a primary aliphatic amine, chitosan can be protonated by various acids[2-4].

By virtue of several valuable inherent properties such as antibacterial, antifungal, antiviral, antacid, non-toxic, total biodegradable, biocompatible with animal and plant tissues as well as film formation, fibre formation and hydrogel formation properties, chitosan has prospective applications in many fields such as biomedical, waste water treatment, cosmetics, dentifrices, food, agriculture, pulp & paper, and textile industries[5-7].

In textiles, the application potential of chitosan is reviewed comprehensively[8,9]. Investigations have shown that it can also be used as a dye fixing agent, for shade and naps coverage, to improve the fastness of dyed fabrics, as a binder in pigment printing, as a thickener in printing. By virtue of its bacteria impeding property, chitosan can prevent garments to develop bad odour[4,8-14]. An improved wrinkle recovery of cotton fabric is reported on finishing cotton with citric acid solution in presence of chitosan with minimum loss in tensile strength due to citric

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acid treatment[15]. It is found that complete inhibition of *Escherichia coli* and Hay bacillus bacteria is possible by treatment of cotton with 0.5gpL chitosan concentration[16]. Tiwari and Gharia[17] attempted to use chitosan as a thickener in printing paste. Performance of the prints with respect to *K/S*, wash fastness, crock fastness and hand are observed to be unsatisfactory. Our earlier investigations[18] have shown improved dyeability towards direct dyes of Chitosan pretreated cotton fabric and the degree of improvement was found to be a function of molecular weight and concentration of chitosan. The fastness to washing of direct dyes on chitosan pretreated fabric, however, was only slightly improved especially for the low molecular weight chitosan applications. Chitosan treated cotton fabric also showed a substantial dyeability towards acid dyes. The appearance and handle of the treated fabric, however, was severely affected. The wrinkle recovery property was found to be reduced. The loss in inherent qualities of cotton fibres due to chitosan may be attributed to the rigid film deposition of it, mostly confined to surface of fibre only.

Today's need, however, is to improve above properties without altering the inherent natural qualities of cotton. It is possible by achieving the maximum penetration of polymer particles into fibre structure and increasing its effectiveness at lowest possible concentration. Penetration of chitosan solution can be improved by lowering the viscosity of its solution, which is obtained by lowering the concentration and/or by reducing the particle size. Reduction in concentration of normal chitosan in solution, however, may reduce its effectiveness and larger chain does not permit its entry into the yarn/cellulose structure. The only possible way is to reduce the particle size, which, in addition to decrease in viscosity, offers greater surface area and hence increase the effectiveness of chitosan. This is the basis of today's most popular technology 'nano technology concept'.

The potential applications of nano-chitosan are well demonstrated in medical field particularly in controlled drug delivery systems[19-21]. However, their applications in textiles are not yet well investigated. The practical application of such nano-chitosan to textiles at shop floor level demands suitable technology for the production of nano-chitosan dispersions, characterization and the analysis of stability of standing baths.

Therefore, in the present work, an attempt has been made to set a simple methodology to produce nano-chitosan by ionotropic gelation with pentasodium tripolyphosphate. Chitosans of different molecular weights are obtained by controlled depolymerisation of parent chitosan using nitrous acid hydrolysis and these products are subsequently used for the synthesis of nano-chitosan. The study reported here is the final results of many basic experiments after getting the confirmation of reproducibility. A representative concentration of 1gpL is, therefore, only reported and discussed here to make it as brief as possible and to avoid presenting less important data. The effect of particle size on various properties of nano-chitosan treated cotton fabric, such as appearance, stiffness, absorbency, dyeing behaviour and wrinkle recovery, is discussed. Scanning electron microphotographs of nano-chitosan treated cotton fabric are also analysed.

2 Materials and Methods

2.1 Materials

100% cotton fabric (count 40s x 40s, EPI 142, PPI 72 and GSM 125), ready for dyeing stage, was procured from local process house.

Direct dyes, namely C.I.Direct Red 81 and C.I.Direct Blue 71, were obtained from M/s Colourtex Industries Ltd, Gujarat State, India. Chitosan (CHT1), having degree of deacetylation (DAC) 90% and viscosity 22cPs, was obtained from M/s Mahtani Chitosan Pvt. Ltd., Gujarat State, India. Dimethylol dihydroxy ethylene urea (DMDHEU) was obtained from local process house and other chemicals such as sodium tripolyphosphate (TPP), acetic acid, sodium nitrite, sodium acetate (anhydrous) and sodium hydroxide used were of analytical grade.

2.2 Synthesis and Characterization of Nano-chitosan

Different molecular weight grades chitosans were first obtained by depolymerization of CHT1 by nitrous acid hydrolysis method, which were employed for the preparation of nano-chitosan dispersions as described elsewhere[22]. In general, chitosan was dissolved in acetic acid solution and optimized quantity of TPP was added drop wise with rapid stirring (about 400 rpm) to obtain an opalescent solution. The sample was allowed to stand overnight, filtered through sintered glass filter of porosity grade G3 and preserved in refrigerator. The prepared nano-chitosan was termed as CHT1N. The synthesized nano-chitosan was applied to cotton fabric within 24 hours since the stability of nano-chitosan gets adversely affected with time as discussed earlier[22]. The specifications of different grades of chitosan and nano-chitosan are given in Table 1. The particle size and size distribution of the chitosan were analyzed on

Table 1—Particle size of nano-chitosan as a function of molecular weight

[CHT:TPP:: 1:0.15]

Parent chitosan		Synthesized nano-chitosan	
Sample code	Molecular weight	Sample code	Particle size nm
CHT1	135,839	CHT1N(i)[a]	468.1
		CHT1N(ii)[b]	319.4
CHT2	71,676	CHT2N	271.6
CHT3	38,733	CHT3N	231
CHT4	20,698	CHT4N	195.2
CHT5	11,986	CHT5N	110.74

[a]Obtained by dilution of CHT1N of 2 gpL concentration to 1gpL

[b]Synthesized directly from CHT1 of 1 gpL concentration

the particle size analyzer (Model: Zetasizer Nano ZS90, Make: Malvern Instruments Ltd, UK).

2.3 Treatment of Fabric with Nano-chitosan

Nano-chitosan dispersion (1gpL) was applied onto fabric on a padding mangle with wet pick-up of 70% by two dip- two nip method. After drying the fabric was cured in oven at 150 °C for 4 min. The sample was then washed in the following sequence: rinse → alkali wash (soda ash 1 gpL, MLR 1:50) → hot wash (twice) (85 °C / 20min) → cold wash → dry.

2.4 Test Methods

SEM Study

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

Evaluation of Indices

The samples were evaluated on Spectroscan 5100A (Make: Premier Colorscan) for whiteness index (10 deg / D65 / Hunterlab), yellowness index (2 deg / C/ ASTM D 1925), brightness index (2 deg / C / TAPPI 452 / ISO 2470).

Fabric Stiffness, Tenacity and Absorbency

Stiffness in terms of bending length was measured as per standard ASTM D 1388-96. The tenacity and elongation-at-break of treated and untreated cotton fibres were measured on Stelometer (Make: Eureka Precision Instrument & Co., Coimbatore, India). The breaking load (kg) and elongation-at-break were obtained directly from scale. The samples were then collected and weighed. An average of 5 readings was calculated using following formula:

$$\text{Tenacity (g/tex)} = \frac{\text{Breaking load (kg)} \times 1.5 \times 10}{\text{Sample weight (mg)}}$$

Sample length = 1.5 cm

Absorbency of treated and untreated cotton fabrics was evaluated as per AATCC test method 79-2000.

Fabric Dyeing

The fabric sample was immersed in dye bath maintained at material-to-liquor ratio of 1:40 and containing 1% direct dye, Glauber's salt (20% owf) and soda ash (5% owf). The sample was run in the bath for 15 min at room temperature. Temperature was then raised to 90 °C and dyeing was continued for 60 min. The dyed sample was then rinsed with cold water 3 times, air dried and hot pressed.

In case of nano-chitosan pretreated material the dyeability was also checked after making the dye bath slightly acidic using 0.5 gpL acetic acid after completion of conventional dyeing process. Presence of acid protonate the amino group which enhances further absorption of dyes.

The dyed samples were evaluated for colour strength in terms of *K/S* values on Premier Colorscan (India) make computer colour matching system namely Spectroscan 5100A. The wash fastness of dyed samples was evaluated according to ISO 1.

Crease Recovery Angle and Antimicrobial Activity

Crease recovery angles were measured as per AATCC test method 66-2003.The untreated and treated samples were subjected to soil burial test as per AATCC Test Method 30-2004. After the stipulated period the samples were removed, washed with water and dried in air. The samples were then tested for strength measurement on stelometer.

3 Results and Discussion

3.1 Synthesis and Characterization of Nano-chitosan

Chitosan has fairly long linear structure with rigid conformation. The characteristic size of CHT1 hydrodynamic sphere is found to be 401.4 nm. Such a higher particle size offers higher viscosity to the solution. It is possible, for a given molecular size chitosan, to reduce the particle size to nano level by 'bottom-up' approach[23]. Chitosan, by virtue of polycationic nature, undergoes ionic gelationwith polyanions such as pentasodium tripolyphosphate (TPP), ethylene diamine tetra acetic acid (EDTA), etc to form nano-particles. Such particles are stabilized by electrostatic hindrance due to coulombic repulsion between particles of same ionic charges[24,25]. Owing to faster ionic reactions between chitosan and TPP, non-toxic nature of these components[23] and ease of operation, we adopted the gel ionization technique for the synthesis of nano-chitosan particles. The particle size distribution of CHT5N, having particle size 110.74nm, is given in Fig.1. Scaling down the particle size of large polymeric materials to nano level is a big challengeIt is clear from the present study that the molecular weight (Table 1) has a great role in controlling the particle size and by reducing the molecular weight we achieved about 110 nm particle size. It is clear from this investigation that the particle size can be reduced below 100 nm by experimenting with parent chitosan of low molecular weight (lower than 10,000). We believe that the study would act as a platform for further work of this kind and would serve basic information to the future researchers.

3.2 Effect of Nano-chitosan Application on Surface Morphology

The surface morphology of the treated and untreated cotton was studied under scanning electron microscope (Fig. 2). Chitosan exhibits an inherent property of film formation, which is clearly seen as

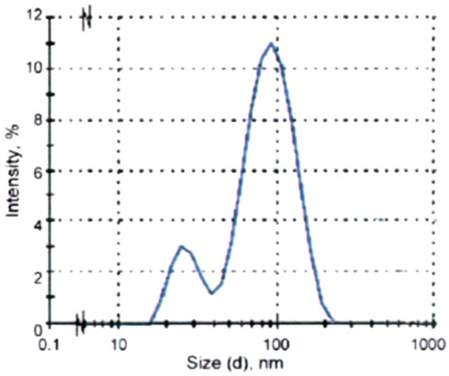

Fig. 1—Size distribution of nano-chitosan by intensity (CHT5N)

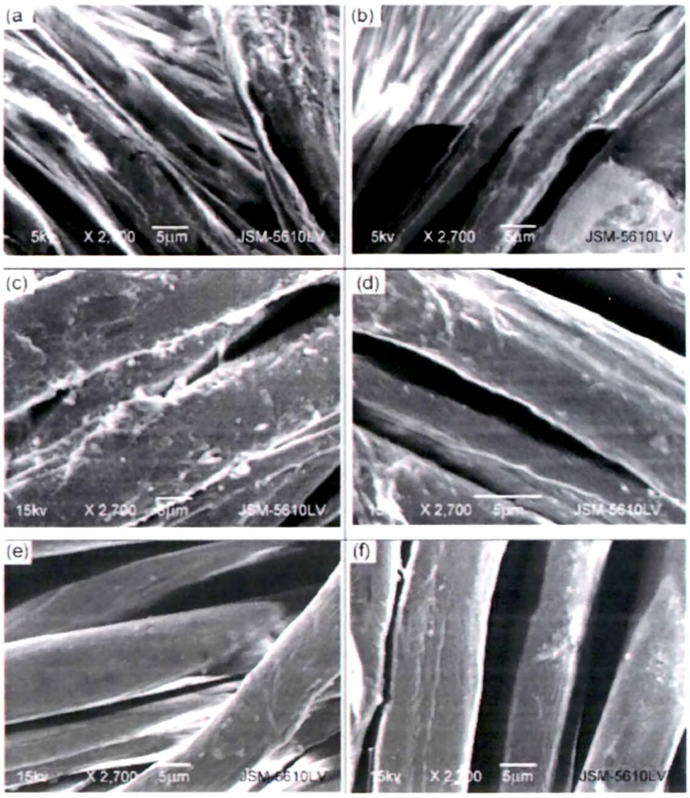

Fig. 2—Scanning electron microphotographs (×2700) of (a) cotton Fibre (control), (b) CHT1 treated fibres, (c) CHT1 treated and then prolong boiled cotton fibres, (d) CHT1N(ii) 319.4nm, treated cotton fibres, (e) CHT4N, 195.2nm, treated cotton fibres and (f) CHT5N,110.74nm, treated cotton fibres

gloss on fibre surface as shown in Fig 2(b). Further, the film deposition on fibre surface can be confirmed by prolong boiling of treated sample in distilled water so that the broken appearance of film can be viewed under SEM [Fig. 2(c)]. Nano-chitosan treated samples show all together different microphotograph [Figs 2(d) – (f)]. Nano-chitosan film is found to be more uniform.

3.3 Effect of Nano-chitosan on Fabric Appearance

The appeal of the fabric is manifested by its appearance and the feel. Effect of particle size of nano-chitosan on these properties of cotton fabric is illustrated in Table 2.

The appearance and the fabric feel are quite satisfactory. It is envisaged from Table 2 that the whiteness is improved with reduction in particle size and reaches well nearer to that of control sample. This may be attributed to the greater extent of penetration of nano-chitosan particles into fibre structure and allowing the cuticle for exposure. Deposition of normal chitosan, however, is confined to surface as a film, which alters the whiteness to some extent. This film may also impart stiffness to the fibre, whereas a nano-chitosan shows a little influence, as is observed in same table.

3.4 Effect of Nano-chitosan on Tensile Properties

The effect of nano-chitosan treatment on tensile properties of cotton fabrics is presented in Table 3.

There is a reduction in strength due to conventional chitosan application. Conventional chitosan mostly forms a film on the surface of the fabric and very less amount of it can enter in to the inter-fibre regions, thus cannot take part in load bearing phenomenon, rather affects symmetrical distribution of load. Nano-chitosan, on the other hand, because of its small size can easily enter into the inter-fibre region and to even inter-cellulosic chain regions, and work as a cross-link which bears the load to a great extent. The strength improvement is therefore clearly observed with the reduction in particle size. The elongation property is, however, decreased to some extent with the scaling down of particle size. The formation of *in situ* three dimensional networks probably resists the adjacent fibre molecules to slip and lowers the elongation-at-break.

3.5 Effect of Nano-chitosan on Absorbency

The absorbency, measured by drop penetration method, of nano-chitosan treated cotton fabric is shown in Fig. 3. The results show that the absorbency is decreased with the reduction in particle size. This may be elucidated by the example of lotus leaf effect. Distribution of nano-chitosan particles as a thin layer over and beneath the surface, [Fig. 2 (d)-(f)], may roll out the water droplets. Nevertheless, the absorbency of nano-chitosan treated samples is still within the tolerable limits of conventional wet processing conditions.

3.6 Dyeing Behaviour of Nano-chitosan Treated Cotton Fabric

Since the structure of chitosan is very much similar to cellulose, it is anticipated that its treatment to cotton should influence the dyeing. Hence, the effect of pretreatment of nano-chitosan on direct dyeing of cotton has been studied. The effects of chitosan and nano-chitosan pretreatment on dye uptake are shown in Table 4. The dye uptake by treated cotton fabric, in conventional process, is increased progressively with reduction in particle size of CHTN. The results are superior to corresponding parent CHT treated materials. The dye uptake of CHTN treated samples is found to be significantly increased, resulting in almost complete exhaustion of dye bath, when acidification was followed. The increased dye uptake due to chitosan treatment may be attributed to the presence of primary amino groups of chitosan. These cations

Table 2—Effect of particle size of nano-chitosan on appearance and stiffness of cotton fabric

Sample code	Particle size nm	Appearance			Bending length, cm	
		W.I	Y.I	B.I	Warp	Weft
Control	-	92.5	2.6	84.6	2.05	1.68
CHT1	401.4	90.9	4.9	81.8	2.44	1.70
CHT1N(i)	468.1	91.1	4.6	82.4	2.29	1.72
CHT1N(ii)	319.4	91.1	4.6	82.3	2.26	1.70
CHT2N	271.6	91.5	3.6	83.4	2.24	1.70
CHT3N	231.0	92.1	3.2	83.7	2.24	1.71
CHT4N	195.2	91.9	3.4	83.8	2.21	1.70
CHT5N	110.74	92.1	3.2	83.8	2.19	1.70

W.I—Whiteness index, Y.I—Yellowness index, B.I—Brightness index dissipate the negative surface charge on cotton and drives dye molecules to the fibre. Further, the dye uptake may also been enhanced due to the dyeability of chitosan itself with direct dyes. The nano-chitosan due to increased surface area and hence higher accessibility for dye sites put much added value. The primary amino groups on chitosan get protonated (quaternized) in acidic medium having enhanced positive charge, thus form salt linkages with anionic (sulphonate) groups of residual dye in the bath. Secondly, the higher dye uptake value after acidification proves the presence of chitosan.

The wash fastness and rub fastness properties of direct dyed fabrics were also analyzed, which are presented in Table 5. The fastness to washing is improved with the reduction in particle size. This may be regarded to the formation of CHTN-dye complex *in situ*. The fastness to rubbing is also improved to some extent with the reduction in particle size.

3.7 Effect of Nano-chitosan on Crease Recovery

The proneness to creasing downgrades the aesthetic appeal of cotton cloth or garments. This problem of cotton fabric is conventionally overcome by the treatment with various cross-linking agents based on

Table 3—Effect of nano-chitosan on tensile properties of cotton fabric
[Control cotton fabric: Tenacity = 23.33 g/tex, Elongation-at-break=5.25%]

Parent chitosan			Nano-chitosan		
Sample code	Tenacity g/tex	Elongation-at-break, %	Sample code	Tenacity g/tex	Elongation-at-break, %
CHT1	20.48	4.75	CHT1N(i)	23.48	4.5
			CHT1N(ii)	25.17	4
CHT2	21.01	4.5	CHT2N	25.61	4
CHT3	21.45	4.5	CHT3N	25.56	4
CHT4	22.19	4.25	CHT4N	25.71	3.75
CHT5	21.81	4.5	CHT5N	25.72	3.5

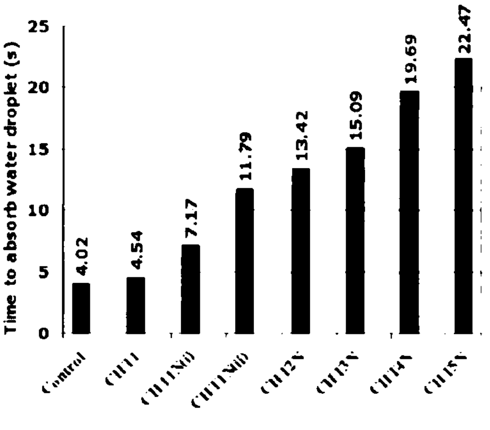

Fig. 3—Effect of particle size on absorbency of treated cotton fabric

Table 4—Effect of particle size of nano-chitosan on dye uptake of treated cotton fabric

Parent chitosan			Nano-chitosan				
Sample code	K/S (Conventional dye bath)		Sample code	K/S*			
				C I Direct Red 81		C I Direct Blue 71	
				Conventional dye bath	Acidic dye bath	Conventional dye bath	Acidic dye bath
CHT1	9.0	6.9	CHT1N(i)	9.6 (24)	10.2 (62)	7.2 (19)	8.0 (63)
			CHT1N(ii)	9.6 (24)	10.4 (64)	7.4 (22)	8.1 (63)
CHT2	9.0	7.0	CHT2N	9.8 (27)	10.5 (66)	7.4 (22)	8.2 (66)
CHT3	9.0	6.8	CHT3N	9.8 (27)	10.5 (66)	7.7 (26)	8.2 (66)
CHT4	9.0	6.7	CHT4N	9.8 (27)	10.5 (66)	7.8 (28)	8.2 (66)
CHT5	9.1	7.1	CHT5N	9.9 (29)	10.6 (67)	7.8 (28)	8.4 (69)

*Values in parentheses indicate per cent improvement in K/S as compared to corresponding control fabric sample
C I Direct Red 81— K/S values of controlled cotton fabric dyed in conventional dye bath is 7.7 and in acidic dye bath it is 6.3
C I Direct Blue 71— K/S values of controlled cotton fabric dyed in conventional dye bath is 6.1 and in acidic dye bath it is 4.9

Table 5—Effect of particle size on fastness properties of direct dyes (conventional dye bath)

Sample code	Particle size nm	C. I. Direct Red 81		C. I. Direct Blue 71	
		Wash fastness	Rub fastness	Wash fastness	Rub fastness
Control	-	3	2-3	4	2-3
CHT1	4014	3	2	4	2
CHT1N(i)	468.1	3-4	2-3	4-5	2
CHT1N(ii)	319.4	3-4	2-3	4-5	2-3
CHT2N	271.6	3-4	2-3	4-5	2-3
CHT3N	231.0	4	2-3	4-5	2-3
CHT4N	195.2	4	2-3	5	3
CHT5N	110.7	4-5	3	5	3

Table 6—Effect of particle size of nano-chitosan on wrinkle recovery property of cotton fabric

Sample code	Pad bath concentration gpL	Particle size nm	Crease recovery angle Å
Control	-	-	161
DMDHEU (40%)	20	-	180
	40	-	207
	60	-	215
CHT1	1	4014	144
CHT1N(i)	1	468.1	158
CHT1N(ii)	1	319.4	162
CHT2N	1	271.6	162
CHT3N	1	231.0	163
CHT4N	1	195.2	165
CHT5N	1	110.7	170

aminoplast resins, e.g. DMDHEU[24]. The crease recovery property as a function of chitosan and nano-chitosan treatments has been compared against DMDHEU (Table 6). The crease recovery angle of cotton fabric is greatly reduced by the treatment of normal chitosan (CHT1). Treatment of cotton fabric with chitosan of lower particle size is found to improve the crease recovery of cotton fabric (Table 6). However yet it could not gain the rating of commercially used cross-linking agent DMDHEU. Conventional chitosan is believed to form a surface coating which lowers the possibility of cross-linking and therefore cannot contribute to the load sharing phenomenon. The improved wrinkle recovery property in case of nano-chitosan treatment may be attributed to the greater penetration into fabric structure. These polycationic nano-particles, due to better penetration, may bound the fibre molecules and resist creasing to some extent.

Table 7—Effect of nano-chitosan treatment on resistance towards microbial attack

Sample code	Tenacity, g/tex		Change in strength from untreated cotton fabric[a], %
	Before soil burial	After soil burial	
Control	23.33	18.98	-18.65
Cotton[b] (Blank treated)	20.87	18.08	-22.5
CHT1	20.48	19.47	-16.55
Ag nano	22.68	22.20	-4.84
CHT1+ Ag nano	24.51	20.27	-13.10
CHT1N(ii)	25.17	21.84	-6.39
CHT1N(ii)+Ag nano	24.21	22.94	-1.67
CHT5N	25.72	22.38	-4.07
CHT5N+Ag nano	25.67	23.03	-1.29

[a] -ve sign indicates the loss in strength

[b] Cotton (blank treated): Acetic acid (15 gpL) applied by pad-dry-cure method.

3.8 Effect of Nano-chitosan on Antibacterial Effect

Cotton fibres like other natural fibres provide favourable environment for the growth of microorganisms due to moisture and warmth. These organisms are mainly responsible for discolouration, development of rancid/bad odour, stains and strength loss of fabric as well as skin allergies and infection diseases to human body[26,27]. One of the most popular ways of imparting antimicrobial resistance is to use nano-silver colloid. Chitosan, being polycationic material, binds to anionic surfaces of microbe cell wall and disrupt it leading to death of cell[8]. Attributing to the antibacterial and metal particle retention properties of chitosan[24], the fabric was treated with chitosan and nano-chitosan and then with nano silver colloid. Nano-silver colloid of concentration $1 \cdot 10^{-3}$ M (100 mL) and average particle size 110nm was prepared as published elsewhere[30].

The resistance against bacterial attack of untreated and treated samples of cotton was determined by measuring the loss in strength due to soil burial test. The results are presented in Table 7. It can be observed that the chitosan can be employed as an efficient antibacterial agent. The effect is enhanced with the reduction in particle size of nano-chitosan and coupling with nano-silver.

4 Conclusion

Ionotropic gelation with pentasodium tripolyphosphate is employed for the preparation of nano-chitosan dispersion. From the stand point application of nano-chitosan to cotton fabric, following conclusions can be drawn.

4.1 The appearance and handle of nano-chitosan treated cotton fabric is quite satisfactory.

4.2 Nano-chitosan treatment shows improvement in fibre strength that increases with the reduction in particle size. The elongation-to-break is slightly decreased with the scaling down of particle size.

4.3 Moisture related property such as absorbency is affected; nevertheless it is in acceptable limit of tolerance.

4.4 The dyeability of chitosan and nano-chitosan treated cotton a fabric towards direct dyes is improved significantly. The progress is sustained with reduction in particle size. The effect is further enhanced after acidification of dye bath. Fastness to washing is improved satisfactorily and fastness to rubbing slightly.

4.5 Wrinkle recovery property is slightly improved and use of suitable cross-linking agent is essential.

4.6 Nano-chitosan together with nano-silver treatment shows enhanced antibacterial activity.

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Studies on Synthesis, Characterization and Viscosity Behaviour of Nano Chitosan

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Abstract

The enhanced performance of chitosan (CHT) treated cotton fabric is anticipated tobe achieved by scaling down the particle size of former to nano level for its greater penetration into the fabric structure. Nano-chitosan (CHTN) was synthesized by ionic gelation of CHT and sodium tripolyphosphate (TPP). The sample was characterized by the determination of particle size and polydispersity index (pdi) on particle size analyzer. Effect of various parameters such as molecular weight and concentration of CHT, concentrations of TPP on particle size were studied. Low molecular weight chitosans were prepared by nitrous acid hydrolysis method and the molecular weights were determined viscometrically. Attempts were made to correlate the viscosity behaviour with particle size of chitosan. The storage stability of CHTN dispersions was studied by periodic evaluation of their viscosity.

Keywords: Chitosan, nano-chitosan, characterization, viscosity behaviour, storage stability.

Introduction

The biopolymer based cationic polysaccharide, chitosan, is obtained by alkaline deacetylation of chitin which is widely distributed in shells of crustacean like lobsters, shrimps, crabs etc. Chemically, chitosan is a linear (1-4) linked 2- amino-2-deoxy-β- d- glucan (i.e. β- d-glucosamine) having the structure very much close to that of cellulose except the hydroxyl group in C (2) of cellulose is being replaced by amino group in chitosan. Indeed, it is a copolymer of N-acetyl-glucosamine and glucosamine units[1-3].

The potential use of chitosan in textiles and various allied fields has attracted strong interest for the development of its several derivatives and colloidal particles of nano level[4-8]. This has been attributed to its valuable inherent properties such as antibacterial, antifungal, antiviral, antacid, non toxic, total biodegradable, biocompatible with animal and plant tissues as well as film formation, fiber formation, hydrogel formation. It is totally eco friendly and renewable[2-9]. Macromolecular chitosan, however, encounters several challenges while its applications to textiles, in particular. Investigations have shown that the inherent properties of cotton fabric such as appearance and handle and other essential properties like fastness of dyes to various agencies due normal chitosan treatment were found tobe affected[10]. These detrimental effects of chitosan are mainly attributed to its lack of penetration into fabric structure causing the surface deposition of film [11,12]. One possible way to enhance its effectiveness is to reduce the particle size closer to nano level, which facilitates the greater penetration of CHT into fabric structure.

The applications of nano chitosan are well demonstrated in medical field particularly as controlled drug delivery systems[13-16]and water treatment for removal of heavy metals[17] and highly pollutant organic compounds like alkyl phenols[18]. However, very few applications nano chitosan in textiles are addressed. Lee et al[19] obtained chitosan and PVA-Chitosan blended submicroscopic fibres by electro spinning method having the average diameter of 200-400 nm. Nano chitosan can be loaded with metal ions such as Ag, Cu, Zn etc to enhance its antibacterial property, as reported by Du et al[20]. The practical applications of nano chitosan to textiles at shop floor level needs suitable technology for its productions, characterization and the analysis of its stability in standing baths. The present work was, therefore, aimed at finding out a simple method of synthesising nano chitosan by ionotropic gelation with sodium tripolyphosphate (TPP) and with the objective to its applications to cotton textiles. The characterization was done by the determination of particle size and polydispersity index (pdi) on particle size analyzer. Chitosans of different molecular weights, obtained by controlled depolymerisation of parent chitosan with nitrous acid hydrolysis, were used for the synthesis of nano particles. The effects of particle size on the viscosity behaviour and the storage stability of their sols are reported.

Material and Methods

Materials: Chitosan (CHT1), having DAC value 90% and viscosity 22cPs, was kindly supplied by M/s Mahtani Chitosan Pvt. Ltd., Gujarat State, India. Other chemicals used such as sodium tripolyphosphate (TPP), acetic acid, sodium acetate (anhydrous), methanol, sodium hydroxide etc were of analytical grade of reputed brands.

Synthesis of low molecular weight chitosan: Different molecular weight grades chitosans were obtained by depolymerization of CHT1 by nitrous acid hydrolysis method as described elsewhere[21]. In general, a 2 % solution of chitosan in acetic acid was prepared. Predissolved dilute solution of sodium nitrite was then added gradually to chitosan solution and stirred for two hrs at 30°C to get desired viscosity level. The depolymerised chitosan was then precipitated out by caustic solution and washed to neutral pH. The precipitates of chitosan was then washed thrice with methanol and dried at 60°C. The molecular weights of these samples were determined viscometrically[illegible].

Synthesis of nano-chitosan and its characterization: Nano-chitosan dispersions were obtained as described elsewhere[21]. However in general, chitosan (CHT1) was dissolved in acetic acid solution and optimized quantity of TPP was added drop wise with rapid stirring (about 400 rpm) to obtain an opalescent solution. The sample was allowed to stand overnight and filtered through sintered glass filter of porosity grade G3 and preserved in refrigerator. The prepared nano-chitosan was nomenclatured as CHT1N.

The particle size and size distribution of the chitosan were analyzed on the particle size analyzer (Model: Zetasizer Nano ZS90, Make: Malvern Instruments Ltd. UK).

Determination of viscosity: The viscosity behaviour of chitosan solution and nano-chitosan sols were studied using Ubbelohde capillary viscometer (No 1A) at 30°C having flow time for distilled water, T = 15.57 seconds.

Results and discussion

Synthesis and characterization of nano chitosan: Chitosan has fairly long linear structure with rigid conformation. These long molecules in solid state are, mostly, in the form of tightly folded random coils. Individual molecular coils are also not discrete and separate but are interpenetrating and entangled with each other. In solution, the solvent gradually diffuse into the polymer aggregates resulting into the swelling of the polymer. As swelling continues, the segments of the polymer are solvated and loosened out as bunches of entangled molecules, known as "hydrodynamic" sphere or ellipsoid[illegible]. The characteristic size of CHT1 hydrodynamic sphere, in our case, at 1 gpl concentration was determined to be 4014 nm. Such higher particle size offer higher viscosity to the solution. It is possible, for a given molecular size chitosan, to reduce the particle size to nano level by "bottom-up" approach as a result of a self assembling or cross linking processes in which the molecules arrange themselves in to ordered nano scale structure either by physical or covalent inter- or intramolecular interactions[illegible]. By virtue of primary amino groups, chitosan under goes Schiff's base formation with aldehydes such as glutaraldehyde, salicylaldehyde etc giving chemically cross linked leading to a quite stable matrices of nano chitosan[illegible]. In another kind of reaction, chitosan hydrogels are obtained by ionic gelation, where nano particles are formed by means of electrostatic interactions with polyanions such as pentasodium tripolyphosphate (TPP), ethylene diamine tetra acetic acid (EDTA) etc. Such particles are stabilized by electrostatic hindrance due to coulombic repulsion between particles of same ionic charges[24,31]. Several other methods of synthesis of nano chitosan such as desolvation method, emulsion-droplet coalescence method, reverse micellar method, self-assembly via chemical modification, spray drying[15,34], and nonaqueous electrochemical method[illegible] are described in literature. Owing to faster ionic reactions between chitosan and TPP, non toxic nature of these components[illegible] and ease of operation, we adopted the gel ionization technique for the synthesis of nano chitosan particles. The intramolecular cross linking in chitosan molecule by gel ionization is schematically illustrated in figure 1. The particle size distributions of various samples of CHTN are presented in figure 3.

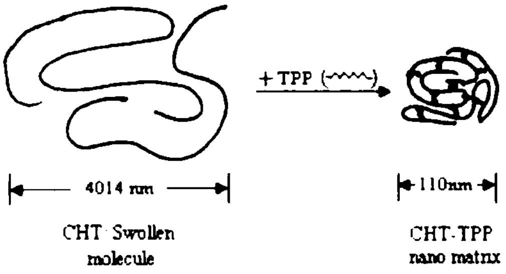

Figure-1
Ionic cross linking of chitosan

Effect of molecular weight of chitosan on particle size: Various grades of low molecular chitosan were produced by controlled depolymerization of high molecular weight one, namely CHT1. When chitosan solution is treated with nitrous acid produced from acidic solution of sodium nitrite, it undergoes deamination reaction with subsequent cleavage of β-glycosidic linkages[illegible]. The IR spectra of chitosan and depolymerised chitosan of different molecular weights determined in earlier study[illegible] were found to be almost similar indicating that the process of depolymerisation caused no significant chemical changes in their structures. These low molecular weight chitosan derivatives were employed for the synthesis of nano chitosan dispersions.

The influence of molecular weight of chitosan on particle size is presented in table 1 and the graphical correlation between intrinsic viscosity, a function of molecular weight, and particle size of nano chitosan is shown in figure 2. These data illustrate that, under a given condition of concentrations of CHT and TPP, with decrease in molecular weight, the particle size also decreased progressively and followed a curvilinear relation. It is well documented[illegible] that the higher the molecular weight or the larger the molecular size, comparatively larger will be the nanomatrix and vise-versa. This relation of particle size with molecular weight in a definite condition of parameters may be useful for synthesis of nano chitosan of desired particle size.

Table-1
Effect of molecular weight on particle size

Parent Chitosan		Synthesized nano chitosan	
Sample Code	Molecular Weight, Mv	Sample Code	Particle size (nm)
CHT1	135,839	CHT1N	319.4
CHT2	71,676	CHT2N	271.6
CHT3	38,733	CHT3N	231
CHT4	20,698	CHT4N	195.2
CHT5	11,986	CHT5N	110.74

CHT:TPP:: 1:0.15

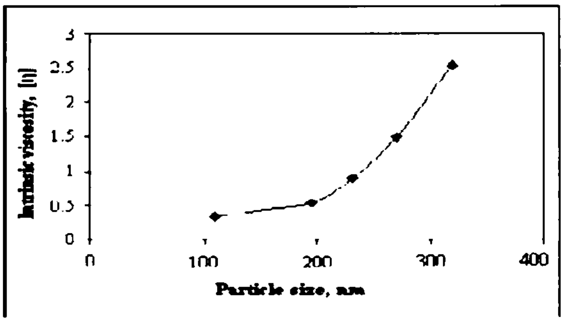

Figure-2
Particle size of chitosan as a function of intrinsic viscosity

Effect of concentration of chitosan on particle size: Two methods were employed for the synthesis of different concentrations of CHTN dispersions namely direct preparation method and dilution method. In first i.e. direct preparation method, the dispersions of nano chitosan from CHT1 of different concentrations such as 0.25, 0.50, 1.0 gpl etc were prepared separately and in the latter, higher concentration nano chitosan dispersion (2 gpl) was prepared first and then diluted to the required concentration with rapid stirring. The effects of these two methods on particle size are presented in table 2. It was observed that at higher concentration, in both the cases, the particle size of CHTN was comparatively large and progressively reduced with the lowering of concentration. The former method, however, was more effective in scaling down the particle size. The larger size of CHTN at higher concentrations may be due overlapping and intermolecular cross linking through TPP bridging resulting into aggregation of polymer molecules. Intramolecular cross linkages in polymer molecule due to TPP at low concentrations, on the other hand, are likely tobe favored for lower particle size. This table also manifests that the poly dispersity indices (pdi) of direct prepared samples were comparatively lower and independent while in dilution method the values were higher and seemed to follow the starting material. The particle size distribution curves, as illustrated in figure 3, were broader for higher concentration samples and became narrow for lower concentration samples. Further, these bands were comparatively narrow for directly prepared samples indicating the uniform size distribution and are close agreement with their lower pdi values.

Effect of TPP concentration on particle size: In ionic gelation reaction, TPP a major ingredient for cross linking has a pronounced effect on the properties of CHTN dispersion. It was observed that with increase in the concentration of TPP the appearance of the system changed from clear viscous liquid to opalescent fluid and then precipitated. The effect of TPP concentration on the particle size is demonstrated in figure 4. At concentration of TPP below 0.05 g, very few phosphate ions were present to produce effective ionic linkages with chitosan amino groups, hence, the solution was clear. As the concentration of TPP was increased gradually, the solution became opalescent indicating the formation of nano chitosan. It was revealed from the same figure that with increase in concentration of TPP, the particle size of CHT1-TPP nanomatrix decreased, reached to minimum at about 0.25 g of TPP and then increased. Concentration of TPP above 0.50 g resulted precipitation. The precipitation at excessively higher concentration of TPP may be attributed to the aggregation of chitosan molecules due to excessive cross linking through TPP bridging. Similar trend in terms of viscosity was noticed when the relative viscosity was plotted against TPP concentration, figure 5.

Table-2
Effect of preparation method and concentration of chitosan on particle size

Direct preparation method			Dilution method		
CHT1 (gpl)	Particle size (nm)	Poly dispersity index (pdi)	CHT1N (gpl)	Particle size (nm)	Poly dispersity index (pdi)
0.25	304	0.421	0.25	347.3	0.465
0.50	313.5	0.441	0.50	354.9	0.471
1.00	319.4	0.422	1.00	468.1	0.515
1.50	408.73	0.441	1.50	516.43	0.515
2.00	534.2	0.515	-	-	-

(CHT1: TPP :: 1:0.15)

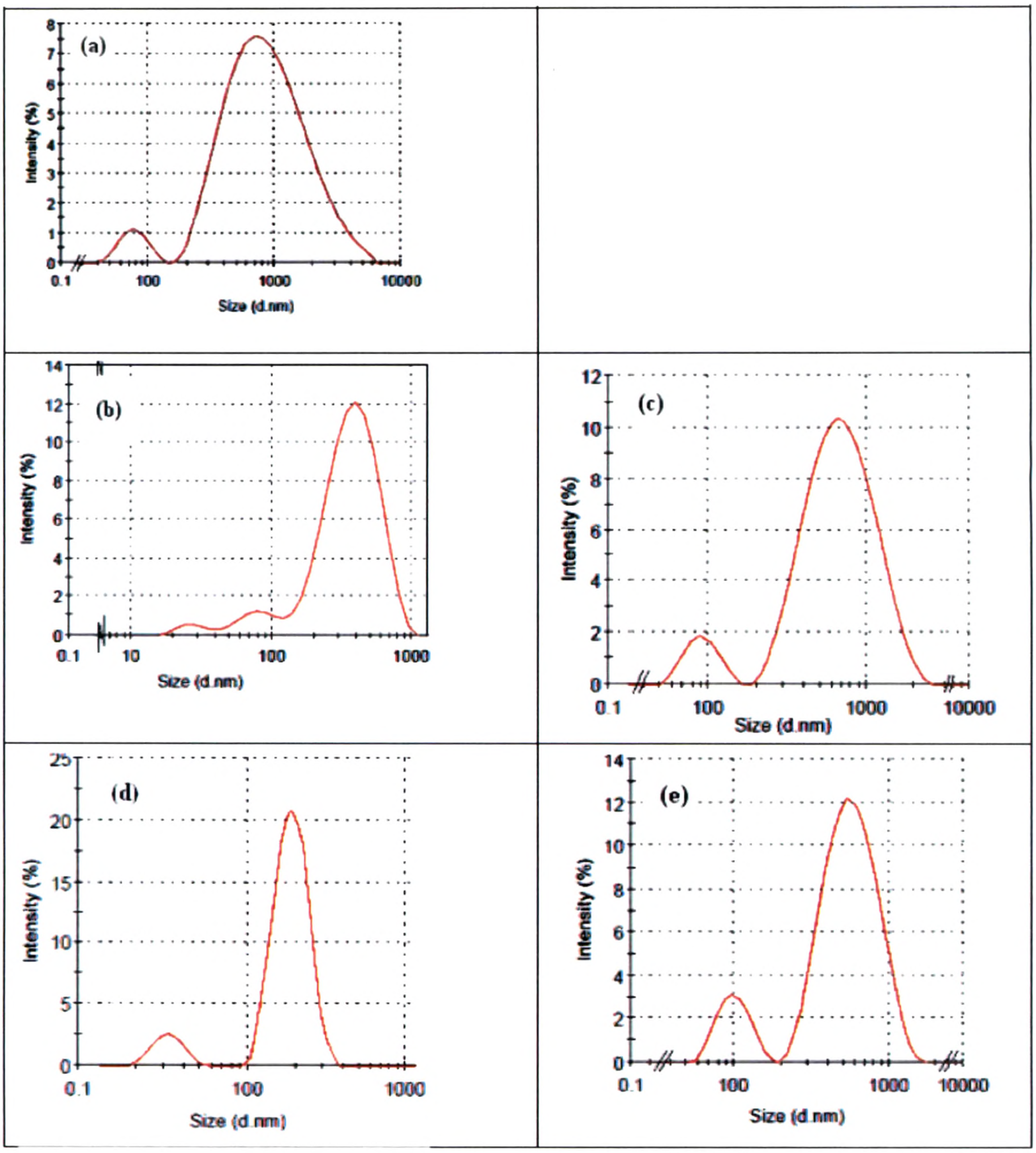

Figure-3

Particle size distribution of nano chitosan as a function of preparation methods: (a)Direct Method: 2gpl (534.2nm), (b) Direct Method: 1gpl (319.4nm), (c) Dilution Method: 1gpl (468.1 nm), (d) Direct Method: 0.5gpl (313.5nm), (e) Dilution Method: 0.5gpl (354.9 nm)

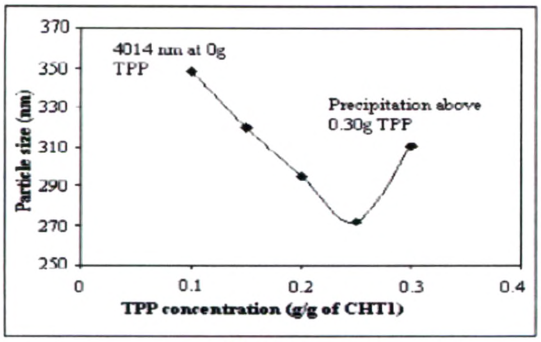

Figure-4
Effect of TPP concentration on particle size of CHT1

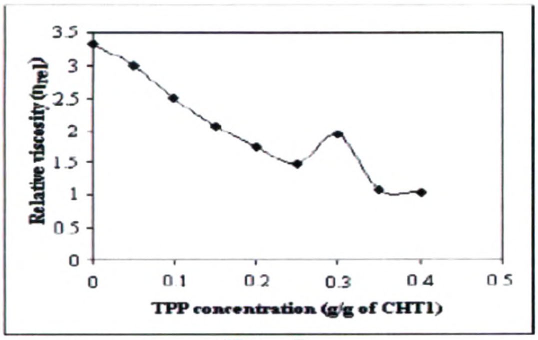

Figure-5
Relative viscosity CHT1 nano solution as a function of TPP concentration

Viscosity behaviour of nano chitosan: The viscosity of polymer solution, at the molecular level, is a direct measure of the hydrodynamic volume of the polymer molecules which in turn is governed by the molecular size or the chain length and hence the molecular weight[25]. Relative viscosity as a function of particle size and the extent to which a parent chitosan scales down to nano level at a given concentration of CHT and TPP are presented graphically in figure 6 and figure 7 respectively.

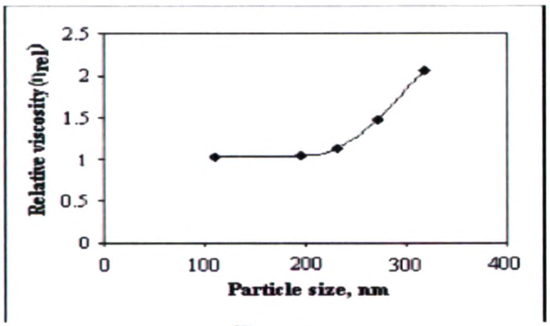

Figure-6
Viscosity as a function of particle size of CHTN

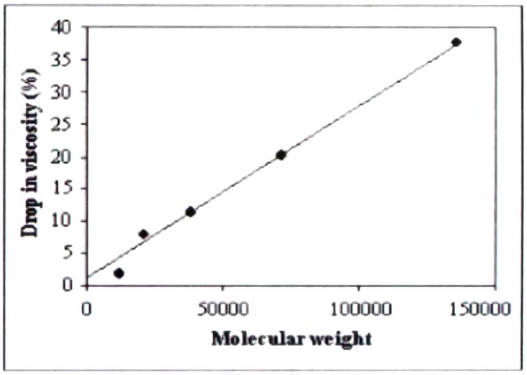

Figure-7
Drop in viscosity from parent (CHT) to nano chitosan (CHTN) solution as a function of molecular weight

It was revealed from figure 6 that the viscosity of CHTN dispersion decreased with reduction in particle size. However, the effect was more significant for larger particles than the smaller one. Obviously, the larger the particle size the higher will be the resistance offered for the flow of liquid and hence the higher will be the viscosity and vise versa. Comparatively slower fall in viscosity for small CHTN particles may be attributed to the low molecular weights of parent chitosan. It is demonstrated in figure 7 that the percentage drop in viscosity from molecular (CHT) solution to corresponding nano chitosan (CHTN) dispersion follows a straight line. It means higher molecular weight chitosan scales down to nano size to greater extent than the lower molecular weight chitosan. This can be explained as follows; large size chitosan molecules in solution accommodate comparatively more amount of solvent and occupy large 'hydrodynamic' volume. These swollen molecules compress to greater extent by ionotropic intramolecular cross linking with TPP by displacing the solvent, as demonstrated in figure 1. On the other hand, the extent of swelling of low molecular weight chitosan is comparatively less[24] and hence lesser will be its tendency to compress.

Stability of nano chitosan dispersion: The biodegradability of chitosan is anticipated to be influenced by its particle size. Therefore the stability behaviour of standing baths of nano chitosan dispersion should be taken into consideration during its applications particularly to textile fabrics. The stability of nano chitosan dispersions for 24 hrs were analysed by viscosity measurements as shown in table 3. The data illustrate that the stability in terms of change in viscosity of parent chitosan (CHT) solution is governed by its molecular weight, which is improved with decrease in molecular weight. The stability behaviour of nano chitosan (CHTN) dispersion, on the other hand, was found to be different from that of parent chitosan solutions. Nano chitosan dispersions obtained from higher molecular weight chitosans are found tobe more stable than the corresponding parent chitosan solutions. Where as the nano dispersions obtained from low molecular weight chitosans are seen tobe more susceptible to degradation. Complete biodegradation of nano chitosan dispersion, in general, was resulted in 3-4 days showing the formation of white globules as shown in figure 8. Therefore, utilization of nano chitosan dispersions in textile applications within the 24 hrs is advisable. Viscosity analysis and visual observations may be the useful tools for stability inspections.

Table-3
Stability of nano chitosan solution as a function of particle size

Parent chitosan(CHT) solution (1gpl)			Nano chitosan solution(CHTN) (1gpl)		
Sample Code	**Molecular Weight, Mv**	**Change in viscosity (%) after 24 hrs**	**Sample Code**	**Particle size (nm)**	**Change in viscosity (%) after 24 hrs**
CHT1	135,839	-10.27	CHT1N	319.4	-3.68
CHT2	71,676	-4.1	CHT2N	271.6	-1.05
CHT3	38,733	-2.6	CHT3N	231.01	-1.18
CHT4	20,698	-2.15	CHT4N	195.2	-3.6
CHT5	11,986	-1.73	CHT5N	110.74	-2.27

Figure-8
Stability study: white globular residue formed by microbial attack on CHT1N

Conclusion

Ionotropic gelation method for the preparation of nano chitosan dispersion using TPP is faster, convenient and non toxic. The concentration of chitosan in the formulation bath has the influence on the particle size. Particle size reduces with decrease in concentration. Direct preparation method gives much reduced size than that of dilution method. With decrease in intrinsic viscosity and hence the molecular weight, the particle size also decreases progressively and shows a curvilinear dependence on particle size. This relation may be useful in preparation nano chitosan dispersion of desired size. TPP concentration determines the particle size. With increase in concentration of TPP, the particle size reduces, reaches to minimum and again increase. Excessive TPP in system leads to precipitation. By reducing the particle size to nano level, the viscosity of chitosan solution is lowered significantly, but the storage stability was affected adversely. Use of freshly prepared nano-chitosan dispersions prior to applications may be the remedy.

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Research Article

Aqueous Behaviour of Chitosan

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Chitosan, a versatile biopolymer, finds numerous applications in textile processing unit operations such as preparation, dyeing, printing, and finishing. However, the accessibility of this biopolymer by the textile material depends on the viscosity of its solution which in turn is a function of its molecular weight. In this work, therefore, the effect of molecular weight, storage life, presence of electrolyte, and particle size of chitosan on its viscosity was investigated. Chitosan of different molecular weights was synthesized by nitrous acid hydrolysis of parent chitosan solution. The synthesized low molecular weight products were analysed by FTIR spectroscopy. Chitosan of nanoconfiguration was prepared by ionotropic gelation method and characterized by particle size analyzer. The viscosity of different chitosan solutions was determined using Ubbelohde capillary viscometer. As an extension to this study, the chelation property of chitosan was also evaluated.

1. Introduction

Chitosan, a versatile biopolymer derivative, is obtained by alkaline deacetylation of chitin. The distribution of the precursor, chitin, in nature is ubiquitous among the shells of crustaceans such as crabs, shrimps, and lobsters as well as in the exoskeleton of marine zoo-plankton including coral, jellyfish, and squid pens. Chemically, chitosan is a linear (1-4) linked 2-amino-2-deoxy-β-d-glucan (i.e., β-d-glucosamine) in the chair $^4C_1$ conformation (Figure 1). The structure of chitosan closely resembles that of cellulose, except an hydroxyl group at C2 position in cellulose being replaced by amino group in chitosan. Indeed, it is a copolymer of glucosamine and N-acetyl glucosamine units. Chitosan exhibits several valuable inherent properties such as antibacterial, antifungal, antiviral, antacid, nontoxic, total biodegradable as well as film formation, fibre formation, and hydrogel formation properties [1, 2]. By virtue of these properties, chitosan has prospective applications in many fields such as medical, waste water treatment, cosmetics, dentifrices, food, agriculture, pulp and paper, and textile industries [3, 4].

In textiles, it finds applications in the primary production of fibres (useful for sutures, wound dressings, etc.), in the manufacture of textile auxiliary chemicals and finishing agents [5–7]. Investigations have shown that it can improve the dye uptake of cotton fibre [8]. It can also be used as a dye-fixing agent, for shade and naps coverage, to improve the fastness of dyed fabrics, as a binder in pigment printing, as a thickener in printing [9]. It is also found that the treatment of wool with chitosan minimizes its felting problem. The bioadhesive and cationic nature of chitosan enables it to form a strongly adhered film on individual fibres and prevent their entanglements [10]. By virtue of its antibacterial property, chitosan can prevent garments to develop bad odour [11–13].

Chitosan when dissolved in acidic solution gives viscous solutions. The viscosity determines the extent of penetration of chitosan into the fabric structure. In solutions, chitosan in suitable conditions shows hydrogel formation and viscoelastic behaviour [14–17]. Its rheological behaviour to characterize its usefulness as thickener in printing paste is reported [18]. However its aqueous behaviour pertaining to various unit operations of textile processing is hardly

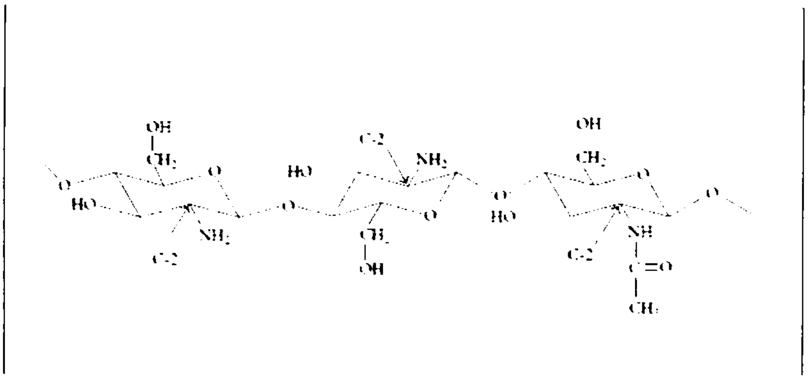

Figure 1: Structure of chitosan.

Table 1: Specifications of different chitosans.

Particulars	Specifications	
Nomenclature	CHT1	CHT3
DAC Value (%)	89.03	90
Viscosity (m Pa·s)	183	22
Molecular Weight	654,127	135,839

reported in the literature. The present research work, therefore, mainly aimed at investigating the aqueous behaviour of chitosan with respect to its molecular weight, concentration and particle size on viscosity and stability of its solution. The effect of electrolytes such as sodium acetate is also reported. The work is also extended to study the chelation behaviour of chitosan.

2. Materials and Methods

2.1. *Materials.* Chitosan samples of different molecular weights were purchased from M/s Marine chemicals, Kerala state, India (CHT1) and M/s Mahtani Chitosan Pvt. Ltd., Gujarat State, India (CHT3). The molecular weights of these samples were determined viscometrically. The specifications of different chitosans are given in **Table 1**.

Other chemicals such as acetic acid, sodium acetate, sodium hydroxide, trisodium polyphosphate (TPP), methanol, and tetra sodium salt of ethylene diamine tetra acetic acid (Na_4EDTA) and used were of analytical grade of reputed companies.

2.2. *Synthesis of Low Molecular Weight Chitosan.* Low molecular weight chitosans were synthesized by controlled hydrolysis of chitosan using nitrous acid as depolymerising agent. A 2% solution of chitosan in acetic acid was prepared. Predissolved dilute solution of sodium nitrite was then added gradually to chitosan solution and stirred for two hrs at 30 °C to get desired viscosity level. The depolymerized chitosan was then precipitated out by caustic solution and washed to neutral pH. The precipitates of chitosan was then washed 3 to 4 times with methanol and dried at 60 °C. The product obtained from CHT1 is termed as CHT2 whereas the products obtained from CHT3 are termed as CHT4 & CHT5.

2.3. *Determination of Molecular Weight and Viscosity.* The molecular weight and viscosity behaviour of chitosan was determined using Ubbelohde capillary viscometer (No 1A) at 30 °C having flow time for distilled water, T_0 = 15.57 seconds. Chitosan solutions of different concentrations in 0.25 M acetic acid and 0.25 M sodium acetate were prepared. During preparation, all the solutions were magnetically stirred for 1 hour to ensure proper dissolution of chitosan and were filtered using Whatman filter paper no 4. The flow times of chitosan solutions and solvent were recorded in triplicate and the average value was calculated. The intrinsic viscosity $[\eta]$ was calculated graphically by extrapolating the curve of reduced viscosity versus concentration to zero concentration. The molecular weight was then calculated by using Mark-Houwink equation (1) [19].

2.4. *FTIR Analysis.* FTIR spectra of chitosan and depolymerised chitosan samples were recorded on a Thermo Nicolet iS10 Smart ITR spectrophotometer (Thermo Fisher Scientific, USA), equipped with an OMNIC-Software, a DTGS detector, and a Ge-on-KBr beamsplitter (4000–500 cm^{-1}).

2.5. *Preparation of Nanochitosan and Its Characterization.* Chitosan (CHT3) was dissolved in acetic acid solution and optimized quantity of TPP was added dropwise with rapid stirring (about 400 rpm) to obtain an opalescent solution containing chitosan 25 mg/dL and TPP 3.75 mg/dL. The sample was allowed to stand overnight and filtered through sintered glass filter of porosity grade G3 and preserved in refrigerator. The prepared chitosan was coded as CHT3N.

The particle size and size distribution of the chitosan were analyzed on the particle size analyser (Model: Zetasizer Nano-ZS90, Make: Malvern Instruments Ltd, UK).

2.6. Evaluation of Metal Ion Chelation Value in Water. The amount of Ca^{+2} as calcium chloride in water for chelation study were determined by volumetric analysis of 50 mL sample against 0.02 M Na_2EDTA solution using Eriochrome black T indicator.

3. Results and Discussion

3.1. Effect of Molecular Weight and Concentration. Chitosan is characterized mainly by two variables, namely, degree of deacetylation (DAC value) and the molecular weight. Degree of deacetylation determines the number of free amino groups present in the chitosan macromolecule, which in turn determines the functionality, polarity, and water solubility of the polymer. On the other hand, molecular weight determines the strength of its fiber/film and viscosity of its solution. Different molecular weight chitosan can be obtained by controlled depolymerization by methods such as acid hydrolysis (HCl, HNO_2, etc.), free radicals (H_2O_2, $K_2S_2O_8$), enzymatic, radiations (UV, γ rays) ultrasound, microwave, and thermal treatments [3, 20–24].

When chitosan solution is treated with nitrous acid, produced from acidic solution of sodium nitrite, it undergoes deamination reaction with subsequent cleavage of β-glycosidic linkages. The reaction scheme and FTIR spectra are illustrated in Figures 2 and 3, respectively.

It envisaged from Figure 3 that the IR spectra of chitosan and depolymerised chitosan are almost similar which indicates that the process of depolymerisation caused no chemical change in the structure of the polymer except reduction in molecular weight which is evident from the change in viscosity.

The viscosity of polymer solution, at the molecular level, is a direct measure of the hydrodynamic volume of the polymer molecules which in turn is governed by the molecular size or the chain length and hence the molecular weight [25]. Therefore, viscosity, measured by capillary viscometer, is widely employed to determine the average molecular weight of a polymer by using the famous Mark-Houwink equation (1)

$$[\eta] = K M_v^{a}, \tag{1}$$

where M_v is the viscosity average molecular weight of polymer, a and k are constants ($a = 0.83$ and $k = 1.4 \times 10^{-4}$ for 0.25 M acetic acid and 0.25 M sodium acetate solvent system) [26] and $[\eta]$ is the limiting viscosity number or intrinsic viscosity and can be determined from [19]

$$[\eta] = \lim_{C \to 0} \frac{(\eta - \eta_0)}{\eta_0 C}, \tag{2}$$

where η is the solution viscosity and η_0 is the solvent viscosity and C is the solution concentration. As indicated in (2), when $(\eta - \eta_0)/\eta_0 C$, that is, reduced viscosity (η_{red}) is plotted against concentration (C), the intercept corresponds to intrinsic viscosity $[\eta]$. Such plots for different grades of chitosan are shown in Figure 4 and the corresponding intrinsic viscosities and calculated molecular weights are presented in Table 2.

Table 2: Intrinsic viscosity and viscosity average molecular weight of different grades of chitosan.

Chitosan	Intrinsic viscosity $[\eta]$, dL/g	Molecular weight, M_v
CHT-1	9.40	654, 127
CHT-2	4.72	285, 231
CHT-3	2.55	135, 839
CHT-4	1.50	71, 676
CHT-5	0.535	20, 698

It can be seen from Figure 4 that the curves of high molecular weight chitosan, namely, CHT-1, 2, and 3, do not strictly follow the linearity of (2). They show the inflection at a certain critical concentration (C^*) and then after the curves bend upwards. Further, the value of C^* increases with decrease in molecular weight and ultimately the curves flatten for lower molecular weight chitosans. This can be explained as follows: when chitosan or any other polymer is added into a solvent, the solvent gradually diffuse into the polymer aggregates resulting into the swelling of the polymer. As swelling continues, the segments of the polymer are solvated and loosened out. Since the molecules in a solid polymer remains entangled with neighbouring ones, polymer molecules during dissolution diffuse out as bunches of entangled molecules. Even when all chain segments of a polymer molecule in solution are unfolded and fully solvated, the molecules do not assume the shape of an extended straight chain but present in a coil form. These coils or aggregates offer resistance for the mobility or flow of molecules and hence impart viscosity [19, 27]. When the molecular size and concentration is increased, as in our case, the extent of entanglement is increased. In other word, the critical concentration (C^*) is, indeed, the "overlap" concentration. When $C > C^*$ the intermolecular entanglements or aggregation, predominate and preclude the overall molecular motion of the polymer, while individual polymer molecules are statistically separated from other molecules at $C < C^*$. Thus, the critical concentration (C^*) is a measure of molecular size and conformation of a polymer. The higher the molecular weight and the more rigid is the conformation, the lower the value of C^*. The results are in close agreement with the earlier reports [15, 28].

3.2. Effect of Storage Time on Viscosity of Chitosan Solution. Polymeric chemicals are generally applied to textiles by padding technique where it is required to prepare a standing bath. Thus the chemical remains in contact with water for a longer period. As biodegradability of chitosan is a well-known phenomenon the effect of storage time on the stability of its solution was studied in terms of change in solution viscosity. It is seen from Figure 5 that the viscosity of chitosan solution is adversely affected with increase in storage time.

It seems that the initial molecular weight and the concentration of polymer has the influence on the stability

$$HNO_3 + H^+ \longrightarrow HNO_2 + Na^+$$

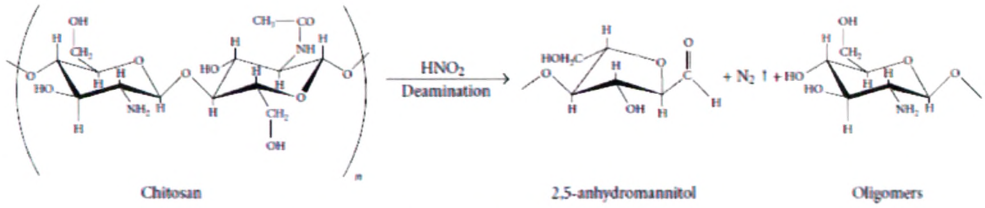

Figure 2: Depolymerization of chitosan by nitrous acid.

Table 3: Chelation property of chitosan.

Treatment	Concentration, gpl	Amount of Ca^{+2} ions (ppm) chelated after:				
		2 hrs	24 hrs	48 hrs	72 hrs	96 hrs
Na_4EDTA	1	405	426	435	450	452
CHT1	1	177	208	232	269	293
CHT3	1	182	187	185	189	196

Initial concentration of Ca^{+2} in water = 625 ppm.

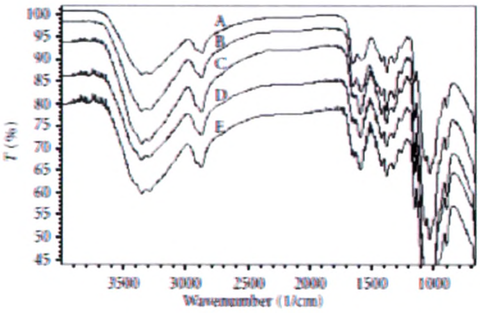

Figure 3: FTIR spectra of CHT1 (A), CHT2 (B), CHT3(C), CHT4 (D) and CHT5 (E).

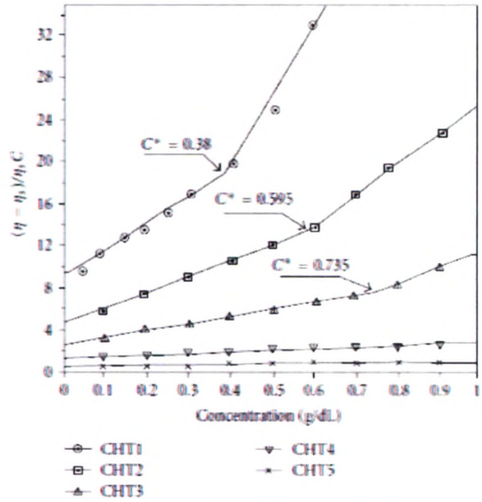

Figure 4: Intrinsic viscosities of different grades of chitosan.

of the solution. Initially the curve shows segments with an overlap concentration (C^*) at the point of inflection and then flattens as the storage time is increased, that is, the critical concentration shifts towards right. It is also observed that the drop in viscosity in first 24 hrs is much faster than the latter and is more significant at higher concentration, that is, above C^*. The loss in viscosity may be attributed to the biodegradation of chitosan molecules and/or hydrolysis of polymer molecules. Initially the large molecules, especially at higher concentration, occupy large "hydrodynamic" volume, which leads to less mobility indicating higher viscosity. The hydrolytic degradation of the polymer leads to the production of smaller molecular entities which in turn causes a drop in hydrodynamic volume of the polymer molecules resulting in higher molecular mobility and as a result reduces the viscosity of the solution [19, 27, 28].

3.3. Effect of Electrolyte on Viscosity of Chitosan. Chitosan is known to be a polycationic material; its solution is believed to be influenced by the presence of electrolytes. Therefore, the effect of sodium acetate concentrations on two different grades of chitosan namely, CHT 1 and CHT 3 was studied.

It can be seen from Figure 6 that the viscosity is sharply reduced in presence of sodium acetate up to a concentration of about 2 g/dL. Further increase in concentration has not influenced the viscosity much. It is also observed that the

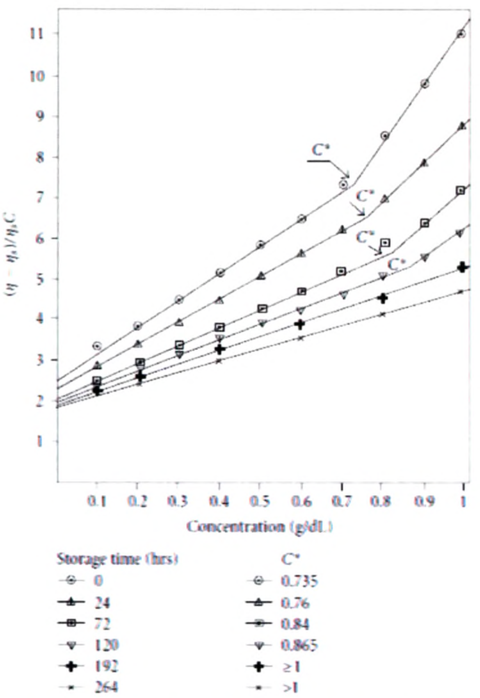

FIGURE 5: Viscosity of chitosan (CHT-3) solution as a function of storage time.

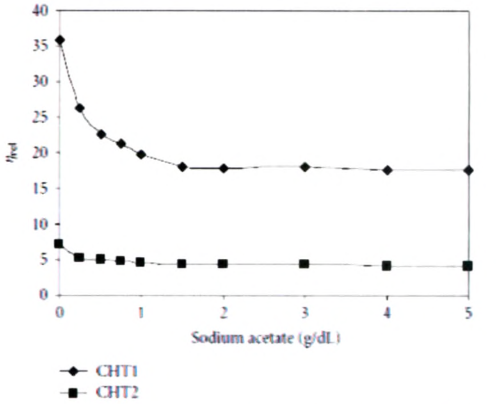

FIGURE 6: Relative viscosity of chitosan solution as a function of electrolyte concentration.

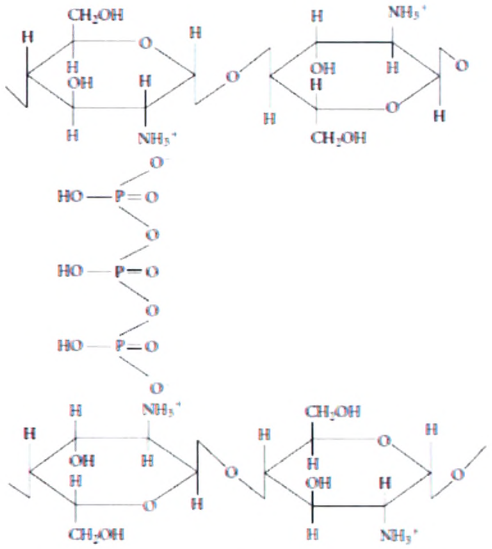

FIGURE 7: Ionotropic cross-linking of chitosan and TPP.

chitosan with higher molecular weight (CHT1) is more affected compared with its lower molecular counterpart (CHT2). The decrease in viscosity with increase in electrolyte concentration can be attributed to the shielding effect of counter ions [29]. Due to ion dipole forces, the acetate ions form a cascade of negative charge over each chitosan molecules establishing repulsive forces between them. This offers low resistance to the flow or mobility of the polymer molecules.

3.4. *Effect of Particle Size on Viscosity of Chitosan.*

It is possible, for a given molecular size chitosan, to scale down the hydrodynamic volume to nanolevel by means of ionotropic gelation using suitable cross linking agent such as sodium tripolyphosphate (TPP), as illustrated in Figure 7. The particles are stabilized by electrostatic hindrance due to coulombic repulsion between particles of same ionic charges [30–32]. We prepared nanochitosan (CHT3N) of average size 394.8 nm from 0.25 gpl CHT3. The particle size distribution and viscosity behaviour of this nanosolution are show in Figures 8 and 9, respectively.

The particle size of chitosan is found to affect its viscosity behaviour significantly (Figure 9). The viscosity of nanochitosan colloid is dropped by about 30% with respect to normal chitosan solution at the same concentration level. The reduction of size to nanolevel has also influenced the stability of chitosan solution. There is 10% drop in the viscosity of normal chitosan for a storage time of 24 hours, whereas nano colloids dropped by 17% for the same storage time. Thus reduction in size reduced the storage stability of the polymer. The reduction in viscosity of nano chitosan solution can be attributed to its lesser resistance towards flow due to its smaller size and enhanced degradation of the polymer in solution due to higher exposed surface area of the nanoparticles.

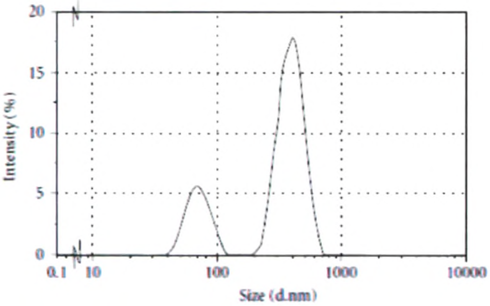

Figure 8: Size distribution of nanochitosan (CHT3N).

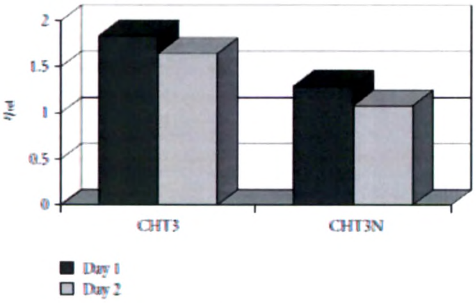

Figure 9: Relative viscosity of chitosan solution as a function of particle size.

3.5. *Chelation Property of Chitosan.* Attributing to the presence of large number of amino groups on chitosan backbone, this biopolymer can also be used in water processing engineering. Chitosan molecules are known to chelate anionic dyes in waste dye solution and flocculate them out.

It has also been found that the chitosan and its derivatives can remove phosphorus, heavy metals, and oils from water [33–37]. In order to study the chelation property of chitosan, the removal of calcium ions from water by CHT1 and CHT3 was determined and the results were compared with Na_4EDTA. Table 3 shows that chitosan can remove the calcium ions substantially though its sequestering power is found to be inferior to EDTA. Further, it is observed that maximum removal occurred in the first 2 hours. Higher molecular weight sample, CHT1 shows better chelation power compared with its lower molecular weight counterpart, CHT3. The former one also shows a continuation in chelation effect even after 96 hrs without reaching the equilibrium, whereas the rest of the samples reached equilibrium within 24 hrs. A substantial higher chelation of Na_4EDTA may be attributed to the combined effect of both carboxylate and amino groups present in its molecule and possibly higher proximity of each molecule due to its relatively small size. The larger molecular size of chitosan provides less surface area and the less amino groups to form the coordinate linkage with calcium ions. The prolonged chelation effect of CHT1 is found probably due to gradual disentanglement of the polymer molecules with respect to time.

4. Conclusions

The viscosity of chitosan is influenced by its molecular weight. Curves of reduced viscosity verses concentration for higher molecular weight chitosan show inflection point, that is, a critical or overlap concentration (C^*). The overlap concentration (C^*) is a measure of molecular size and conformation of a polymer.

The higher the molecular weight and the more rigid is the conformation and lower is the value of C^*. The initial molecular weight and the concentration of chitosan are found to influence the stability of its solution. The drop in viscosity in first 24 hrs is found to be very fast, and the critical/overlap concentration (C^*) point shifts towards right when the storage time is prolonged.

In presence of electrolyte, the viscosity of chitosan solution is reduced, which is found to be more pronounced for high molecular weight chitosan solution.

By reducing the particle size to nanolevel, the viscosity of chitosan solution is lowered significantly, but the storage stability was affected adversely. Use of freshly prepared nanochitosan solution prior to applications may be the remedy.

Chitosan exhibits chelation property. This property is useful in removing metal and dye ions from water.

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Studies on the properties of chitosan treated cotton fabric

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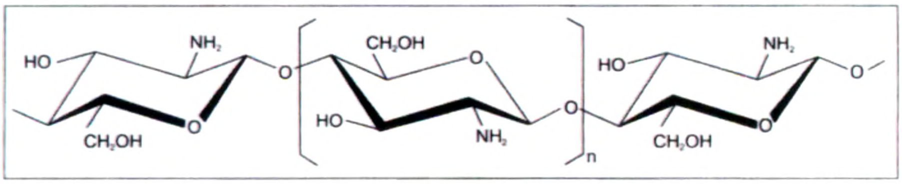
Chitosan is a natural based polymer obtained by alkaline deacetylation of chitin. The precursor, chitin, is widely distributed in shells of crustaceans such as crabs, shrimps, lobsters etc as well as in the exoskeleton of marine zoo-plankton, including coral, jellyfish and squid pens etc with the abundance ranking next to cellulose and is renewable. The structure of chitosan is very much close to that of cellulose except that the hydroxyl group in C(2) position of cellulose is being replaced by amino group in chitosan.It is composed of linear (1-4) linked 2- amino-2-deoxy-β-d-glucan (i.e. β-d-glucosamine) in the chair $^4C_1$ conformation. Indeed, it is a copolymer of N-acetyl-glucosamine and glucosamine units.

Chitosan can be taken as a valuable wet processing agent, but faces several challenges while exploring its applicability.

Chitosan is a white fibrous material produced in different grades according to the degree of deacetylation and molecular weight. Chitosan, being a primary aliphatic amine, can be protonated by various acids. It is insoluble in water, organic solvents and alkalies, but is soluble in organic acid solutions[1,2,3].

Chitosan exhibits several valuable inherent properties such as antibacterial, antifungal, antiviral, antacid, non toxic, total biodegradable as well as film formation, fibre formation, hydrogel formation etc. By virtue of these properties, chitosan has prospective applications in many fields such as biomedical, waste water treatment, cosmetics, dentifrices, food, agriculture, pulp and paper, and textile industries[4,5,6,7,8,9].



Chitosan

In textiles, it finds applications in the primary production of fibres (useful for sutures, wound dressings etc), in the manufacture of textile auxiliary chemicals and finishing agents. Investigations have shown that it can be used as a dye fixing agent, for shade and naps coverage, to improve the fastness of dyed fabrics, as a binder in pigment printing, as a thickener in printing etc. By virtue of its bacteria impeding property, chitosan can prevent garments to develop bad odour [2,5,10,11,12,13,14,15]. Tahlawy[16] studied the effect of chitosan in the finishing of cotton with citric acid in presence of sodium hypophosphite catalyst. He reported a recovery of losses (due to citric acid treatment) in dye uptake and tensile strength, and improved wrinkle recovery by the addition of chitosan in citric acid bath. The whiteness index, however, was deteriorated. In a similar study, Chung et al[17] showed, besides improved wrinkle recovery and D P rating, a high antimicrobial property level which retained through twenty washing and tumble drying cycles. Zhang et al[18] conducted an experiment to study the effect of concentration, molecular weight and degree of deacetylation of chitosan on antibacterial activity to Escherichia coli and Hay bacillus bacteria. They reported a complete inhibition of these bacteria at 0.5 gpl chitosan concentration. They also observed the increased reduction rate of bacteria with increase in molecular weight and degree of deacetylation. Tiwari and Gharia[19] attempted to use chitosan as a thickener in printing paste. Performance of the prints with respect to K/S, wash fastness, crock fastness and hand were observed to be unsatisfactory. Similar attempts were made by Bahmani et al[20] to use chitosan in pigment printing. They showed the prints of satisfactory colour fastness to rubbing, washing and light; however, the major problems were the poor colour value and stiffness of the printed fabric. These suggest that the modification of chitosan is desired. Dutta et al[21] and Abdel-mohdy et al[22] found chitosan to be useful in effluent treatment by virtue of its adsorbing qualities of dyestuffs and various heavy metal ions. In a recent work, modified chitosans' application to cotton made it possible to dye cotton in absence of salt with much higher dye exhaustion compared to the conventional dyeing using recommended quantities of salt[23]. Young Ho Kim et al[24] synthesised quaternary ammonium derivative, N-(2-hydroxy)propyl-3-trimethyl ammonium chitosan chloride by using a reaction of glycidyltrimethylammonium chloride with chitosan. They were able to obtain 100% bacteria reduction at only 0.025% of this derivative as against only 30% bacteria reduction at 1% chitosan. Pourjavadi[25,26] graft copolymerised chitosan with polyacrylamide and methacrylonitrile using ammonium persulphate initiator in order to impart desired properties to chitosan such as superabsorbancy, controlled drug release etc. Grafting can also be carried through hydroxyl groups while protecting the useful amino groups on chitosan backbone. Gorochovceva et al[27] successfully grafted polyethylene glycol at hydroxyl groups through the cynuric chloride bridging.

In this paper, research findings on the effect of applications of chitosan on the dyeing and finishing properties of cotton have been reported. The chitosan was used both as a pre- and post-dyeing agents to investigate its effect on the dyeability and fastness properties of cotton with various direct dyes. The effect of chitosan pre-treatment on the dyeability towards acid dye was also investigated. This biopolymer was used as a finishing agent with an intention to incorporate crease resistant property to cotton. Its effect was compared with the commercially available wrinkle resistant agents and also examined its compatibility with them. The molecular weight of chitosan governs the viscosity of its solution and hence the extent of penetration into the fabric structure. The studies were, therefore, extended to chitosan of varying molecular weights.

Materials and methods

- Fabric : 100% cotton fabric (Count: 40's X 40's, EPI: 142, PPI : 72 and GSM: 125), ready for dyeing stage, was procured from local process house. All preparatory processes such as desizing, scouring, bleaching, mercerising etc were given in factory itself
- Dyes : Different acid and direct dyes were obtained from M/s Colourtex Ind Ltd, Surat (Gujarat) :
  - C I Acid Blue 158
  - C I Direct Red 81
  - C I Direct Blue 71
- Chitosan : Chitosan samples of different molecular weights were purchased from M/s Marine Chemicals, Cochin (Kerala) and M/s Mahtani Chitosan Pvt Ltd, Veraval (Gujarat). The molecular weights of these samples were determined viscometrically[28].

Table 1 : Specifications of different chitosans

Particulars	Properties	
Supplier	M/s Marine Chemicals, Cochin (Kerala)	M/s Mahtani Chitosan Pvt Ltd, Veraval (Gujarat)
Product Code	C1	C2
DAC Value (%)	89.03	90
Viscosity (cps)	183	22
Molecular weight	6, 54, 127	1, 35, 839

The specifications of different chitosans are given in *Table 1*.

DMDHEU (40%) was obtained from local process house and other chemicals such as acetic acid, sodium acetate (anhydrous), sodium hydroxide, sodium nitrite, methanol etc used were of LR grade of reputed brands.

Depolymerisation of chitosan

Depolymerisation of chitosan was carried out by sodium nitrite. 2 % solution of chitosan (C2) in acetic acid was prepared. Predissolved dilute solution of sodium nitrite was then added gradually to chitosan solution and stirred for two hrs at 30 C to get desired viscosity level. The depolymerised chitosan was then precipitated out by caustic solution and washed to neutral pH. Chitosans of two different low molecular weights obtained were coded as follows

Product code	Molecular weight
DC1	71,676
DC2	38,733

Fabric treatment with chitosan

Required amount of chitosan was dissolved in solution containing acetic acid 15 gpl and sodium acetate 10 gpl, and applied to fabric on a padding mangle with wet pick-up of 70% by two-dip two-nip method. After drying, the fabric was cured in oven at 150 C for 4 mins. The sample was then washed in the following sequence:

Hot wash (Twice) [85 C 20mins] - Alkali wash [Soda ash 10 gpl, MLR 1:50] - Hot wash - Cold wash - Dry

Dyeing with direct dyes

The fabric sample was dyed with direct dyes with 1% shade at 90 C for 60 mins using dyebath containing 20% Glauber's salt and 5% soda ash. The dyed sample was then rinsed with cold water, air dried and hot pressed.

The dyed samples were evaluated for K/S values and strength on Spectroscan 5100A (Make : Premier Colorscan). The washing fastness of dyed samples was evaluated according to ISO 1.

Dyeing with acid dye

The fabric sample was dyed with acid dyes with 2% shade at 90 C for 60 mins using dyebath containing 1 ml/l acetic acid. The dyed sample was then rinsed with cold water, air dried and hot pressed.

Evaluation of whiteness, yellowness and brightness

The samples were evaluated on Spectroscan 5100A (Make : Premier Colorscan) for whiteness, yellowness and brightness in terms of the corresponding Indices

Whiteness Index (WI)	10 deg D65 Hunterlab
Yellowness Index (YI)	: 2 C/ASTM D 1925
Brightness Index (BI)	: 2 C/TAPPI 452/ISO 2470

Crease recovery angle

Crease recovery angles were measured as per AATCC Test Method 66-2003.

Stiffness of fabric (Bending length)

Bending lengths were measured as per standard ASTM D 1388-1996

Results and discussion

Chitosan is characterised mainly by two variables, namely, degree of deacetylation (DAC value) and the molecular weight. Degree of deacetylation determines the number of free amino groups present in the chitosan macromolecule which, in turn, determines the functionality/reactivity, polarity and water solubility of the polymer. On the other hand, molecular weight determines the strength of its fibre/film and viscosity of its solution. The very high molecular weight and therefore a high viscosity of chitosan solution penetrates less into the fabric structure and hence leads to only surface deposition and alters the fabric feel and appearance. Low molecular weight chitosan often known as chitosan oligomers or chito-oligosaccharides, on the other hand, by virtue of its low viscosity, penetrates to greater extent into the fabric structure. This can offer better durability without much affecting the feel and appearance[29,30]. Therefore, in order to study the chitosan treated cotton textiles, we prepared two different low molecular weight chitosans by depolymerisation.

Various methods of depolymerisation are reported in the literature[4,31,32,33,34,35] such as acid hydrolysis (HCl, HNO_3 etc), free radicals (H_2O_2, $K_2S_2O_8$), enzymatic, radiations (UV, γ rays), ultrasound, microwave, thermal treatments etc. Depolymerisation by acid hydrolysis using nitrous acid (HNO_2) proceeds through deamination reaction with subsequent cleavage of β-glycosidic linkages.

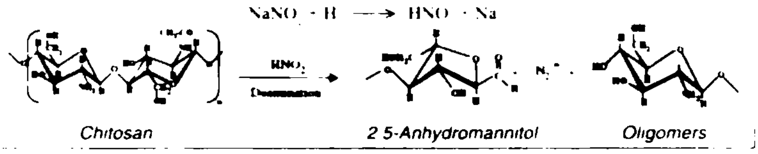
The depolymerisation of chitosan was conducted by nitrous acid hydrolysis method.

Effect of concentration of chitosan on appearance and feel

The viscosity of a polymer solution is also governed by its concentration[36]. The effect of application concentration of chitosan on various physical properties were evaluated and presented in *Table 2* and *Table 3*.

It is observed from *Table 2* that the whiteness and the brightness of chitosan treated fabrics are satisfactory for high molecular weight chitosans but slightly reduced with increase in concentration of chitosan. In general, the whiteness of chitosan is negatively affected due to application of chitosan. The extent of deterioration in whiteness, however, is substantially high in highly depolymerised chitosan i.e. for DC2 at high concentrations. It seems, here, that the excessive depolymerisation by sodium nitrite produces undesired impurities containing aldehyde end groups, which may react with free amino groups to form -N=C bond (Schiff's base) resulting in yellowness[4]. Additionally, the possible liberation of nitric oxide gas from $NaNO_2$ in acidic medium may also enhance the yellowness. A thorough purification of the product may be the remedy.

The fabric stiffness is found to be progressively increased with increase in the concentration and molecular weight of chitosan, as seen from *Table 3*. The



The depolymerisation of chitosan was conducted by nitrous acid hydrolysis method

Table 2 : Appearance of chitosan treated fabric as a function of molecular weight and concentration

Conc	C1			C2			DC1			DC2		
(gpl)	WI	YI	BI	WI	YI	BI	WI	YI	BI	WI	YI	BI
2.5	91.4	3.6	82.4	90.9	3.3	81.6	91.5	3.6	83.4	89.9	3.7	79.8
5.0	91.8	3.6	83.2	90.8	3.4	81.4	91.9	3.6	83.6	89.0	7.4	76.9
7.5	91.4	4.7	82.2	90.4	4.3	80.6	91.5	4.0	82.9	89.2	8.1	76.9
10.0	91.3	4.4	81.9	90.5	4.7	80.6	91.4	4.3	82.6	87.7	9.2	74.2
15.0	90.9	4.9	81.3	90.1	4.5	79.8	91.5	4.7	82.3	86.4	13.5	70.6
20.0	90.2	5.4	79.8	89.2	5.8	77.9	90.3	5.4	79.9	84.1	16.2	66.1

Control : WI = 92.5, YI = 2.6, BI = 84.6

Table 3 : Stiffness of chitosan treated fabric as a function of molecular weight and concentration

Conc	Bending Length, cms							
(gpl)	C1		C2		DC1		DC2	
	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
2.5	2.61	1.76	2.44	1.70	2.33	1.85	2.15	1.60
5.0	2.80	2.10	2.98	2.05	2.58	1.85	2.30	1.71
7.5	3.41	2.55	3.23	2.25	2.68	2.01	2.48	1.86
10.0	4.29	3.03	3.70	2.74	3.05	2.19	2.90	2.00
15.0	4.90	3.23	4.10	3.00	3.39	2.21	3.31	2.38
20.0	5.38	3.53	4.40	3.33	4.06	2.88	3.53	2.68

(Bending length of control sample : Warp = 2.05 cms and Weft = 1.68 cms)

fabric surface was also found to be excessively harsher in case of high molecular weight chitosan. This increased stiffness and harshness may be attributed to the formation of surface coating of stiff film due to very high viscosity of the solution. This property is not desirable in pretreated fabrics but may be beneficial when applied during finishing process, which imparts firmness and body to the fabric. The high viscosity solutions, however, cause difficulties during application in padding mangle.

Absorbency

Rapid and uniform absorbency for any pretreated fabric is indispensable for the better penetration of dyes and chemicals during the subsequent unit operations like dyeing, printing and finishing[37]. Therefore, the effect of chitosan applications on the absorbency was determined, which is shown in *Table 4*.

The absorbency (measured by water drop absorbance time) of chitosan treated fabric is found to be satisfactory. From *Table 4*, it can be observed that average absorbency of high molecular weight chitosan treated fabric decreased slightly with the increase in its concentration; whereas the absorbency of low molecular weight chitosan treated samples is not much affected. The reduction in absorbency in case of former may be due to the formation of rigid film of chitosan over the surface, thus acting as a barrier for the penetration of water.

Table 4 : Effect of molecular weight and concentration on absorbency

Conc of chitosan gpl	Absorbency, seconds			
	C1	C2	DC1	DC2
2.5	5.13	4.54	5.03	7.38
5.0	5.28	4.58	5.03	12.06
7.5	8.44	5.98	6.41	11.43
10.0	12.70	7.20	5.54	9.60
15.0	16.02	7.05	7.05	8.93
20.0	72.28	7.19	7.09	10.13

(Absorbency of control sample : 4.02 secs.)

Dyeing behaviour

Dyeing with direct dyes : Since the structure of chitosan is very much similar to cellulose, it was thought that its treatment may influence the dyeing behaviour of cellulose. In this work, the effect of pretreatment and after treatment of chitosan on direct dyeing of cotton is examined. The washing fastness properties of these samples are also analysed. The effects of chitosan pretreatment on dye uptake, measured in terms of K/S, are shown in *Table 5* and their washing fastnesses are presented in *Table 6*. The effect of chitosan treatment on the shade of dyed fabric and the washing fastness are presented in *Tables 7 & 8* respectively. It is observed from *Table 5* that the dye uptake (K/S), of both the dyes, increased substantially with increase in concentration of chitosan. The dye uptake is also found to be affected by the molecular weight of chitosan.

Table 5 : Effect of chitosan pretreatment on direct dye uptake

Conc of chitosan (gpl)	K/S C I Direct Red 81 C1	C2	DC1	DC2
2.5	9.2	9.4	9.4	9.4
5.0	7.9	9.3	10.9	9.9
7.5	9.4	10.9	10.3	11.3
10.0	10.3	11.3	10.9	12.1
15.0	12.8	12.2	11.8	11.4
20.0	14.7	13.5	13.8	12.1
	C I Direct Blue 71			
2.5	8.6	9.6	9.4	9.4
5.0	9.4	11.6	9.8	9.8
7.5	10.6	10.8	9.8	10.1
10.0	13.4	12.4	10.6	13.0
15.0	18.8	15.6	12.2	14.4
20.0	16.6	16.1	13.8	14.4

(Dye : 1% owf, K/S values of control sample : CI Direct Red 81 = 7.7 and CI Direct Blue 71 = 7.4)

Cotton fabric, when introduced in dye bath, acquires negative surface charge and repels negatively charged dye anions, leading to poorer dye exhaustion as found in case of fabric dyed in absence of chitosan. The increased dye uptake due to chitosan treatment may be attributed to the increased dye affinity towards the positively charged amino groups. This charge dissipates the negative surface charge on cotton and drives dye molecules to the fibre. Further, the dye uptake may also have been enhanced due to the dyeability of chitosan itself with direct dyes.

Table 6 shows that the washing fastness of C I Direct Red 81 is marginally improved with the increase in the concentration of chitosan, particularly in case of relatively low molecular weight chitosan treated samples. On the other hand, for the samples treated with high molecular weight chitosan, there is slight reduction in the wash fastness with increase in the treatment concentration of chitosan. However, the effect of chitosan treatment on washing fastness of dyes with good washing fastness viz C I Direct Blue 71, is not altered appreciably.

It is observed from *Table 7* that the colour value of C I Direct Red 81 is little improved whereas that of C I Direct Blue 71 is little decreased due to the chitosan after treatment. This contradictory result may be attributed to the differences in the washing fastness of these dyes. Easily washable Red dye is migrated to a greater extent from the fabric to the chitosan layer during pad application and further during drying. The washing fastness of post dyeing chitosan treated fabrics is improved *(Table 8)*.

- Dyeing with acid dye : Chitosan possesses an amino group in its glucosamine unit, which forms positive charge in presence of acid. This positively charged amino group can form salt linkage with anions. In order to verify this kind of interaction of chitosan, we carried out the dyeing of chitosan treated cotton fabric with acid dyes. The results are presented in *Table 9*.

It is observed from the *Table 9* that the dyeability towards acid dye is substantial in all grades of chitosan. The dye uptake increased with increase in concentration of chitosan. This kind of dyeability can be purely attributed to the binding of acid dye to chitosan by salt linkages. The untreated (control) sample showed merely a tinting effect. Thus, the dyeability toward acid dye can be

Table 6 : Effect of chitosan pretreatment on washing fastness of direct dye

Conc of chitosan (gpl)	Washing fastness ratings C I Direct Red 81 C1 Change in colour	C1 Staining	C2 Change in colour	C2 Staining	DC1 Change in colour	DC1 Staining	DC2 Change in colour	DC2 Staining
5.0	2-3	2-3	3	2-3	3	2-3	3	2-3
10.0	3	2-3	3-4	2-3	3	2-3	2-3	3
15.0	2-3	2-3	3-4	3	3-4	3	3-4	3
20.0	2	2-3	3	3-3	2-3	3	3-4	3
	C I Direct Blue 71							
5.0	4-5	3	4-5	3-4	4-5	3-4	4	3-4
10.0	4	3	4-5	3-4	4	3-4	4-5	3
15.0	4	3	4-5	3-4	4	3	4-5	3
20.0	4-5	3	4-5	3-4	4-5	3-4	4-5	3

(Washing fastness ratings of control samples : CI Direct Red 81 : Change in colour = 3 & Staining = 3; CI Direct Blue 71 : Change in colour = 4-5 & Staining = 3-4).

Table 7 : Effect of post-dyeing chitosan treatment on colour depth of direct dyed fabric

Finish Treatment	Conc (gpl)	K/S	
		C I Direct Red 81	C I Direct Blue 71
Control	-	6.6	7.3
C1	5	6.8	7.2
	10	7.2	7.5
C2	5	7.2	6.8
	10	7.5	7.3
DC1	5	6.9	6.8
	10	7.2	7.1
DC2	5	7.2	6.6
	10	6.9	6.6

(Concentration of dye = 1% owm)

Table 8 : Effect of post-dyeing chitosan treatment on washing fastness of direct dye

Finish Treatment	Conc (gpl)	C I Direct Red 81		C I Direct Blue 71	
		Change	Staining	Change in	Staining
Control	-	3	2	4-5	3
C1	5	3	2-3	4	4
	10	3-4	2-3	4-5	4-5
C2	5	3-4	2-3	4-5	4
	10	3-4	3	4	4-5
DC1	5	3-4	3	4-5	4
	10	3-4	3	4-5	4-5
DC2	5	3-4	2-3	4-5	4-5
	10	4-5	3	4-5	4-5

Table 9 : Dyeing of chitosan pretreated cotton with acid dye, C I Acid Blue 158

Conc of chitosan (gpl)	K/S Value			
	C1	C2	DC1	DC2
2.5	1.7	1.5	1.6	2.0
5.0	1.6	2.1	2.3	2.4
7.5	2.3	3.0	2.8	3.5
10.0	3.1	3.8	3.7	3.0
15.0	4.4	4.9	4.9	5.5
20.0	6.1	7.7	6.5	6.3

(Shade : 2% owf, K/S value of control sample : 0.3831)

Table 10 : Wrinkle recovery property of chitosan treated cotton fabric

Conc of chitosan (gpl)	(Crease recovery angle)°			
	C1	C2	DC1	DC2
Control	161	161	161	161
2.5	137	140	140	176
5.0	143	140	160	164
7.5	129	119	152	141
10.0	94	125	138	128
15.0	96	110	127	134
20.0	90	98	116	121

(CRA of control sample = 161°)

taken as one of the characterisation tests for the retention of chitosan on cotton fabric.

Wrinkle recovery property

One of the major drawbacks of cotton textiles is its tendency to crease. Various cross linking agents such as UF, DMU, DMEU, DMDHEU etc resins are employed to overcome this problem. The wrinkle recovery property of chitosan treated fabrics was compared with DMDHEU. The results of this experiment are shown in *Table 10 and Table 11*.

Table 11 : Wrinkle recovery property of DMDHEU treated cotton fabric

Conc of DMDHEU (40%) (gpl)	(CRA)°
Control	161
20	180
40	207
60	215
80	226
100	233

It is seen from *Table 10* that the wrinkle recovery of chitosan treated cotton fabrics is not satisfactory. Rise in application concentration of chitosan has greatly reduced the wrinkle recovery of cotton. However, low concentration of lower molecular weight chitosan application has improved the crease recovery angle. The high molecular weight chitosan is believed to form mostly a surface coating which lowers the possibility of cross linking and therefore cannot contribute to the load sharing phenomenon.

Conclusion

The appearance of cotton fabric, in terms of whiteness/brightness, is affected due to the chitosan application. The stiffness and harshness of chitosan treated fabric also increased with increase in the molecular weight and concentration of chitosan. Chitosan treatment has not affected the absorbency of cotton much. The dyeability of chitosan treated cotton fabrics towards direct dyes is improved significantly; it is increased with increase in molecular weight and concentration of chitosan. However, the washing fastness of direct dye on chitosan pretreated fabric is only slightly improved, especially for low molecular weight chitosan applications. The effects of post-dyeing treatment for different dyes are different. However, the post-dyeing chitosan treatment, in general, has improved the washing fastness of direct dyed cotton fabric.

Chitosan can, therefore, be taken as a valuable wet processing agent, but yet faces several challenges while exploring its applicability. Therefore, an extensive research in this area is the need of the hour.

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Bayer MaterialScience ends reduced working hours at German sites

Effective November 1 this year, Bayer MaterialScience (BMS) will be reverting to the standard collectively agreed work week of 37.5 hours at its German sites. At the beginning of February, the company had introduced a reduction in working time and a corresponding pay reduction of 6.7% to combat the effects of the financial crisis. An opening clause in the collective agreement was applied in order to avoid short-time working. With the reintroduction of normal working hours, the rates of pay for some 4,100 employees will return to their normal level.

"The reason for lifting this special arrangement is the improvement in orders. Nevertheless the future business development of our customer industries still remains uncertain," said Dr Tony Van Osselaer, labour director at Bayer MaterialScience AG. Short-time working would mainly have affected employees in production. "Thanks to the solidarity of all our employees, this was prevented," said Thomas de Win, chairman of the central works council of Bayer AG. Managerial employees of Bayer MaterialScience were also affected by the cuts, which in their case included the cancellation of this year's round of pay increases.

Similar measures were also taken at the international sites, adapted in each case to their economic situation.

Chitosan and its Versatile applications in Textile Processing

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Chitosan, a polysaccharide obtained by the deacetylation of chitin, is a versatile agent used in the primary production of textile fibre, textile auxiliary chemicals and textile finishing agents. Besides its textile applications, it has got a number of other useful uses. In medicine, it is used to make artificial skin and blood vessels, surgical suture, anti-tumour agent, immunity promoter, anti- cholesterol agent etc. In food industry, it can be used as stabilizer and thickener. In daily use chemical industry, it can be used as hair fixer and hair conditioner, and many more. It seems that a number of applications of this polymer are yet to be discovered. Because of the potentiality of this polymer scientists from different fields have been attracted to explore its uses in their respective fields. In this paper, various aspects of chitosan and its textile applications are briefly reviewed.

Key words: Chitin, chitosan, chemistry, properties, applications.

INTRODUCTION

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

Ecological considerations, now days, are becoming important factors in the selection of consumer goods, all over the world. The consumers demand not only the right quality product, at right time, at a reasonable price, but also with no harm to ecology during the manufacture as well as in the use. Hence, there has been a constant urge to scientists and industrialists to explore and adopt the substitutes, that are non-hazardous and ecofriendly.The use of natural dyes on textiles has been one of the consequences of increased environmental awareness. Enzymes are commercially available for the processes like desizing, scouring, bleaching, and finishing. Eyes are, today, focused towards biopolymers to minimize the use of hazardous synthetic polymers in textile processing. One such promising example of this kind is CHITOSAN (Pronounced as kite-o-san), which is derived from naturally occurring polymer CHITIN (kite-in).Both chitin and chitosan are biopolymers and are biodegradable, biocompatible with animal and plant tissues, non toxic, and renewable.

Chitin, the precursor of chitosan, is a nitrogen containing polysaccharide and is second most abundant biopolymer after cellulose. It is widely distributed in the shells of crustaceans such as crabs, shrimps, lobsters etc as well as in the exoskeleton of marine zoo-plankton, including coral, jellyfish and squid pens. About 20-40% chitin is present in the exoskeleton of these animals. It is also present in smaller quantities in insects such as butterflies, ladybugs, and the cell walls of yeast, mushrooms and other fungi. But since the crustacean shells (crabs etc) are waste products (now byproducts) of food industry, these are commercially employed for production of chitin and chitosan it is believed that at least ten gigatons (10^{13} Kgs.) of chitin are synthesized and degraded and it is also estimated that over 1,50,000 tons of chitin is available for commercial use annually[1,2,3]

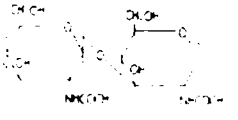
BRIEF HISTORY OF CHITIN AND CHITOSAN

Prof. Henri Braconot, Director of Botanical Garden in Nancy (France) in 1811, first isolated a fraction from the cell walls of mushroom, which he called FUNGINE. Later in 1823, Odier discovered that this compound is also one of the major constituent of the exoskeleton of insects and then he renamed as CHITIN (meaning tunic or envelope in Greek) Prof C Rouget in 1859 prepared a compound from chitin by treatment with concentrated caustic solution This compound was then named as CHITOSAN by Hoppe Seiler in 1894 However the existence of chitosan in nature was discovered in 1954 in the yeast Phycomyces blakesleeanus

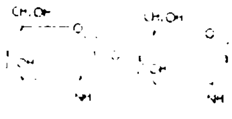
Over past decades researchers in Korea Japan Europe and USA have tested chitin and chitosan in biomedical applications In Japan chitosan was first used for waste water treatment to absorb grease oils heavy metals and other potentially toxic substances Researchers claim that a tooth paste made from crab's shell could cut dental infections and reduce the number of visits to dentists [3 4]

CHEMISTRY OF CHITOSAN

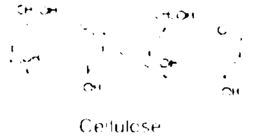
Chitosan [$(C_6H_{11}O_4N)_n$] is a polysaccharide composed of a linear (1 4) linked 2 amino-2-deoxy-β- d- glucan (i e β- d-glucosamine) in the chair $^4C_1$ conformation It is derived by deacetylation of chitin i e (1-4) linked 2 acetaamido-2-deoxy β d glucan (i e N-acetyl- β- d-glucosamine) Indeed it is a copolymer of N-acetyl-glucosamine and glucosamine units The structure of chitosan is very much close to that of cellulose except the hydroxyl group in C (2) of cellulose is being replaced by amino group in chitosan This is evidenced by I R and ^{13}C NMR spectroscopy The average molecular weight determined by the viscosity measurement methods is of the order of 5×10 The structures of chitin chitosan and cellulose are as below



Chitin



Chitosan



Cellulose

Chitosan mainly occurs in two molecular conformations namely (i) as extended two fold helix and (ii) as extended eight-fold helix The eight fold helix conformation transforms into two-fold helix under high humidity No ordered conformation however is present in the aqueous acidic solution The molecular flexibility increases with increase in deacetylation increase in ionic strength in the solution and increase in temperature [5 6 7 8 9 10 11 12]

PRODUCTION OF CHITOSAN

Chitosan can directly be isolated from some fungi mainly Phycomyces blakesleeanus (yeast) Zygomycetes etc species However the yield is too low To date chitosans have been produced commercially by the alkaline deacetylation of crustaceans chitins

The crustacean shells mainly consist of chitin (20-30%) proteins (30-40%) Calcium Carbonate (30-50%) lipids and traces of pigment The proteins are removed by treatment with dil sodium hydroxide (about 10%) at about 85 C to 100 C or digested enzymatically by proteases or micro-organism The shells are then dematerialized to remove calcium carbonate by the treatment with dil hydrochloric acid (about 10%) at room temperature Lipids are extracted by soaking in organic solvents such as acetone or ethanol An oxidative bleaching treatment with hydrogen peroxide or sodium hypochlorite is also given to obtain a white powder

Squid pens are also the potential source of chitin and chitosan Squid-pens are removed from the squid during processing and are currently regarded as waste so the raw material is cheap Since the squid pens are very low in calcium, the acid extraction step is not required This in turn reduces the cost and acid hydrolysis of chitin Therefore comparatively cheaper and better quality chitin can be produced

Conversion of chitin into chitosan involves the deacetylation process, which is a harsh treatment usually performed with concentrated sodium hydroxide solution Chitin flakes are treated in suspension with aqueous 30 60% caustic solution at 80 - 120 C with constant stirring for 4 6 hours and this treatment is repeated for once or more times for obtaining high amino content product To avoid depolymerization due to oxidation, sodium borohydrate is added Deacetylation of chitin can also be done enzymatically Here powdered chitin is treated with N-deacetylase (EC 3 5 1 41) or with microbes which secrete N-deacetylase The enzymatic method yields chitosan with low degree of N acetylation and low degree of polymerization

The degree of acetylation of chitosan may be determined by C N ratio (by elemental analysis) by ^{13}C NMR by ^{15}N NMR by I R Spectroscopy by colloidal titration and by pyrolysis gas chromatography In general chitosans have nitrogen content higher than 7% and degree of acetylation lower than 0 40 [4 13 14 15, 16 17 18 19]

PROPERTIES OF CHITOSAN

Chitosan is a white fibrous material (also available as beads and membranes), produced in different grades according to the degree of deacetylation (D D) and the molecular weight Various factors such as source of chitin and processing parameters while conversion of chitin into chitosan determines the grades of chitosan

Chitosan being a primary aliphatic amine can be protonated by selected acids (pK of chitosan 6 3) It is insoluble in water organic solvents and alkalies but is soluble in or ganic acid solutions. In aqueous solutions, above certain polymer concentration, intermolecular interactions lead to the formation of associations thus exhibiting properties .The viscous solution shows Newtonian flow.

Under particular conditions, chitosan can give highly hydrophilic water swellable hydrogels. One of the simplest ways to prepare chitosan gel is to treat chitosan acetate solution with carbamide.The gel formation is also promoted by adding cross linking agents or organic solvents.

Chitosan also possesses film formation property. The films are mostly flexible with smooth and shiny surface. The quality of film depends on the source from which the precursor 'chitin' is obtained. The films of quid-pen chitosan are clearer and rigid than that of crab and cray fish chitosan [11,12,14,20,21,22].

Chitosan has two hydroxyl functional groups at 3rd and 6th carbon atoms and one amino functional group on 2nd carbon atom. The amino functional group imparts strong positive charge to chitosan which allows it to bind negatively charged surfaces such as skin, hairs, textiles etc.The cationic nature of chitosan also helps to bind cholesterol and clotting of R.B.C. Further, this amino group gives usual chemical reactions such as acetylation, quaternization, reactions with aldehydes and ketones (to give Schiff's base) alkylation, grafting, chelation of metals etc . Chitosan is readily depolymerized by acidic sodium nitrite to give oligosaccharide. The hydroxyl functional groups also give various reactions such as o-acetylation, H-bonding with polar atoms, grafting etc [23,24,25,26,27,28,29,30].

Chitosan also exhibits several valuable inherent properties such as anti bacterial, anti fungal, anti viral, anti acid, anti ulcer, non toxic, non allergenic, total biodegradability etc and hence finds wide applications in diverse fields such as waste water treatments, food, medical, biotechnology, agriculture, cosmetics, pulp & paper, plastic and textile industries. Over 250 applications are known at present [3,31,31,33,34,35].

Some of the applications of chitosans in the area of textiles are discussed in the following sections.

CHITOSAN FIBRES

Owing to the linear structure, chitosan exhibits fibre forming property.Chitosan filaments also known as crabyon (crab + rayon) are produced by wet spinning method. Chitosan is dissolved in acetic acid solution and then extruded through the spinneret into a caustic co-agulation bath to obtain a regenerated fibre. However, such fibres have poor wet strength (tenacity 2.0 gpd) .Investigations have shown the improved tenacity of up to 4.4 gpd by incorporation of surfactants into the coagulation bath. Such fibres find use in the production of textiles having antimicrobial, antithrombogenic, hemostatic, deodorizing, moisture controlling, and non allergenic properties which are inturn used as bandages for wound- dressing, as sutures, as perfume releasing fabrics.

A composite material of chitin/chitosan and cellulose are produced by mixing powder chitin/chitosan with viscose pulp and then wet spun.These fibers have high moisture keeping property than cellulosic fibres and have dyeability towards direct and reactive dyes. These fibres are used as textile materials for under wears, socks, etc as these keep skin from drying. At the same time, these give velvet touch and no irritation to skin .Therefore: clothes made up of these fibres are excellent for babies and old aged people who have weak and sensitive skin [3, 10, 35, 36, 37, 38].

APPLICATIONS OF CHITOSAN IN TEXTILE PROCESSING

DYEING

Cotton and other cellulosic fibres, conventionally, are dyed with direct, reactive, vat, reactive, azoic etc dyes, which are anionic in nature. Cotton also acquires negative surface charge when immersed in dye baths of above dyes leading to repelling action to them. To dissipate this -ve surface charge and to facilitate the dyeing, large amount of electrolytes such as common salt or Glauber's salt are added into the dye bath. These electrolytes and unexhausted dyes add to the pollution load when discharged through effluents. Such high salt dissolved water can neither be useful for agriculture purpose nor be recycled for industrial uses. Moreover, the available technique of reverse osmosis (R.O.) to reduce the T.D.S.is not yet economically viable. Thus attempts have been made to adopt salt free and alkali free dyeing by cationization of cotton by treatment with glycidyl trimethyl ammonium chloride, N, N-dimethyl azetidinium chloride (DMAAC), N-methylol acrylamide (NMA), chloropropionyl chloride (CPC) etc. However, the question of ecological aspects arises here too. As a solution, modification of fibre with chitosan could be a best option.

The fabric is pretreated with chitosan by pad-dry-cure method using cross linking agents such as polycarboxylic acid (e.g. butane tetra carboxylic acid or citric acid) or N-methylol compounds (e.g. DMDHEU). Investigations have shown several valuable results such as: increased dyeability of cotton toward direct and reactive dyes in absence of salt, dyeability toward acid dyes, elimination of colour difference between matured and immatured cotton, coverage of neps etc.It is believed that, chitosan acts as built-in catalyst of reactive dyes in question with hydroxyl groups of cotton and chitosan. Very recently, it has been revealed that a complete salt-free dyeing of cotton with a lot of saving in the quantity of dyes is possible by simple modification of chitosan and its application to cotton material [12,20,28,39,40,41,42].

PRINTING

Chitosan solution on drying gives a colourless, transparent and flexible film having smooth surface. These films are wash fast when fixed on fabric by thermofixation. Further, chitosan exhibits thickening properties. Thus, by virtue of these properties, chitosan can be used in pigment printing to replace the conventional synthetic binders which are based on styrene-butadiene, styrene-acrylates, or vinyl acetate-acrylate co-polymers [11,43].

WOOL TREATMENT

Wool, due to its scaly structure, exhibits felting problem as a result of frictions arising during various wet processing operations. The penetration of dyes and chemicals through the fibres/yarns is, thus, hindered. Conventionally, the felt formation is prevented by descaling process with treatments such as chlorine, enzymes (protease) etc.The chlorine treatment, however, is not ecofriendly and causes tendering of the fibres.Where as, the second one requires exact control of parameters and is not enough to fulfill the woolmark requirements. Recently, investigations have shown reduced felting of wool when treated under plasma. This process, however, is not economically viable due to prolong treatment time and high cost.

Treatment of wool with chitosan has been found to minimize this felting problem. The bio-adhesive and cationic nature of chitosan enables it to form a strongly adhered film on individual fibres and prevent their entanglements. The extent of adsorption and uniformity of distribution of chitosan onto the fibre can be increased by increasing the wettability and anionic character of fibre. Alkaline peroxide pre-treatment or oxidative plasma treatment creates new anionic groups such as sulphonate and carboxylate, and improves the wettability of wool fibre and hence the binding power of chitosan. However, such degradative treatments lead to considerable weight loss and damage to the fibre. Treatment of wool with a surfactant containing anionic groups can lead to higher pick up of chitosan causing no damage to the fibre. A combination of controlled enzymatic treatment followed by chitosan treatment can also give satisfactory antifelting effect. Further, these treatments have also shown increased shrink resistance and dyeability of wool towards reactive dyes [11,44,45,46,47].

POLYESTER TREATMENT

Besides several useful essential properties, polyester suffers from one serious drawback of hydrophobicity and consequently the static charge built-up problem. This static electricity is mostly responsible for dust/dirt attraction, sticking of clothes to human skin, increased fibre contamination during textile finishing, overlapping of fabric heat setting on stenter, malfunctioning of electric devices, sparks and ignition of its materials etc. To dissipate such static charges, the fibre surface is coated with an antistatic agent, which is mostly synthetic hydrophilic resins, by simple pad-dry-cure method. However, the effect is not durable. An ecofriendly and durable antistatic finish can be obtained by the treatment of polyester with chitosan. Chitosan has the advantage that it shows high moisture regain even in low relative humidity and does not swell much in water. The finish is more stable on polyester that has under gone a caustic reduction treatment. Here cross linking of chitosan takes place by reacting chitosan-NH_2 group with carboxyl end group of polyester that are generated by caustic reduction process [48,49].

ANTICREASE FINIHING

The creasing problem of cotton is well known, which is attributed to the presence of free hydroxyl groups in the fibre molecules. The creasing problem is minimized by cross linking these free hydroxyl groups on adjacent molecules in the fibre using a suitable cross linking agent such as N-methylol compounds (UF, DMDHEU etc resins). However, these finishing agents suffer from one serious drawback of release of toxic free formaldehyde. As an alternative, on formaldehyde cross linking agents such as citric acid, butane tetra carboxylic acids (BTCA) etc are recommended. Among these, BTCA is most effective cross linking agent; but the cost is very high. Citric acid, although cheaper, is less effective and has drawback of yellowing problem due to the formation of unsaturated polycarboxylic acid (due to dehydration of citric acid). To counteract this yellowness, additives such as hydroxyethyl amines, borates or polyethylene glycols to citric acid bath are recommended. However, the process is still less effective.

The crease recovery power of citric acid can be improved satisfactorily by the incorporation of chitosan in presence of sodium hypophosphite monohydrate (SHP) to the citric acid bath. Here, the esterification reaction not only occurs between citric acid and cellulose but also between citric acid and hydroxyl groups of chitosan and the free carboxylic groups can also react with amino groups of chitosan by salt linkages. Low molecular weight chitosan (obtained by controlled oxidative degradation by sodium nitrite) at low concentrations have shown improved wrinkle recovery without deterioration in whiteness and strength of fibre [12, 20,28,35,50,51].

ANTIMICROBIAL FINISHING

The conventional temporary wound dressing used with antimicrobial cream and ointment is time consuming and patients feel pain because of the frequent replacement of wound dressing. Therefore, the method of drug delivery system has been accepted for full-thickness skin wound care and the antimicrobial agent impregnated wound dressings are proven effective in controlling bacterial invasion through a porous matrix. However, the use of conventional antimicrobial agents such as organo-metallics, phenols, quaternary ammonium salts, organo silicones etc are not desirable due to their toxic nature. In this regard, drug impregnated polyelectrolytes wound dressings composed of chitosan and sodium alginate in sponge form are used. The non toxic, antifungal, antiviral and antimicrobial nature of chitosan accelerate the wound healing and the sodium alginate provides the moist wound atmosphere which promotes healing and epidermal regeneration.

The antimicrobial property of chitosan is attributed to the primary amino group at C-2 position of glucosamine residue. The effect is more enhanced when the amino group is protonated or quaternized. The protonised amino groups block the protein sequences of micro-organisms, thus inhibiting further proliferation. Chitosan binds to the anionic surface of microbe cell wall and disrupt it and alter its permeability. This results material to leak out of bacterial cells causing in cell death. Chitosan also binds to DNA inside the cell inhibiting mRNA and hence protein synthesis.

Also, the antimicrobial treatment of chitosan can be done on various textiles such as cotton, wool etc for preservation and antifungal effects. It also helps odour reduction and perspiration bonding. The antimicrobial finish of chitosan (dissolved with acetic acid) on cotton fabric can be applied by usual pad-dry-cure technique. Incorporation of cross linking agents such as citric acid, glutaric dialdehyde, glyoxal, or DMDHEU etc enhance the chitosan uptake on the surface of cotton fabric with good durability to washing [3,20,35,52,53,54].

EFFLUENT TREATMENT

Textile process houses discharge huge quantities of dyes and chemicals through the effluent. Conventionally, the effluent water is processed by treatment with lime & ferrous sulphate system and/or synthetic polyelectrolytes mostly based on polyacrylamide. Colouring matters and some organic chemicals are flocculated by this method but the TDS value due to inorganic salts is significantly increased leading to increased pollution load. Treating waste water using "greener" methods has become an ecological necessity. The ecofriendly polysaccharide, chitosan, has proved to be the best alternative. Being cationic in nature, chitosan has high affinity for wide range of dyes and other negatively charged particles and flocculate them. Various chitosan polyelectrolytes obtained by reaction polyanions, acidic polysaccharides, and some acidic proteins can be used for effluent treatments [2,11,14,55,56].

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