



Metal complexation by chitosan and its derivatives: a review

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Abstract

One of the major applications of chitosan and its many derivatives is based on its ability to bind strongly heavy and toxic metal ions. This article reviews the various classes of chitosan derivatives and compares their ion binding abilities under varying conditions, as well as the analytical methods to analyze them, the sorption mechanism, and structural analysis of the metal complexes by various methods. Data are also presented exhaustively in tabular form with reference to each individual metal ion and the types of compounds that complex it under various conditions, to help arrive at conclusions regarding the comparative efficacy of various classes of compounds, structure–property relationships, and so on.

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1. Introduction

Chitin, the source material for chitosan, is a high molecular weight linear polymer of 2-acetamido-2-deoxy-D-glucopyranose units linked together by 1,4-glycosidic bonds. It is obtained in large quantities from crustacean shells, which are waste products of seafood processing industries. Chitosan is the *N*-deacetylated product of chitin. Although a sharp nomenclature border does not exist between chitin and chitosan, the term ‘chitosan’ usually represents copolymers of 2-amino-2-deoxy-D-glucopyranose and 2-acetamido-2-deoxy-D-glucopyranose where the degree of deacetylation is generally more than 60%. Unlike chitin, chitosan is soluble in dilute organic acids such as acetic acid, formic acid, lactic acid, etc.

Both chitin and chitosan are becoming increasingly important natural polymers because of their unique combination of properties like biodegradability, biocompatibility and bioactivity, in addition to attractive physical and mechanical properties. Consequently, they have a variety of current and potential applications in biomedical products (Kifune, 1992), cosmetics (Gross, Konrad, & Mager, 1983),

food processing (Knorr, 1985), etc. Metal chelating agents for removal of metallic impurities in wastewaters is an excellent application for large-scale use of chitosan.

Many other materials like fly ash, silica gel, zeolites, lignin, seaweed, wool wastes, agricultural wastes, clay materials, sugarcane bagasse, etc. have also been extensively investigated for the removal of pollutants from aqueous streams, especially for heavy metals like Cd^{2+} , Cr^{3+} , Cr^{6+} , Hg^{2+} and Pb^{2+} . The maximum adsorption capacities of chitosan for Cd^{2+} , Cr^{3+} and Hg^{2+} were shown to be 558, 92, 1123 mg/g of chitosan, respectively, which were higher than that of other materials studied (Bailey, Olin, Bricka, & Adrian, 1999). Sugarcane bagasse and its oxidized product can bind Cu^{2+} , the adsorption capacity being 0.1292 mmol/g for bagasse (Filho, Winkler-Hechenleitner, & Gomez-Pineda, 1996). Also, lignin from bagasse can bind Cd^{2+} and Pb^{2+} (Petternele, Winkler-Hechenleitner, & Gomez-Pineda et al., 1999).

It is also reported that chitosan has the highest chelating ability in comparison to other natural polymers obtained from seafood wastes (Yang & Zall, 1984) and natural substances like bark, activated sludge and the synthetic polymer poly(4-aminostyrene) which is used in commercial chelating ion-exchange resins (Masri, Reuter, & Fiedman, 1974). Chitosan has binding capacities of more than 1 mmol/g for heavy and toxic metals, with the exception

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of chromium, and is more efficient in scavenging Ni^{2+} from industrial waste as compared to other natural materials like polymerized peanut skins. Indeed, waste-water containing 7 ppm Ni^{2+} , after passing through a column of chitosan, showed Ni^{2+} contents of less than 0.1 ppm. Regeneration of the chitosan maybe effected by buffered ammonium chloride (Randall, Randall, McDonald, Young, & Masri, 1979). The ability of chitosan to bind transition metals in the presence of alkali and alkaline earth metals is well-investigated (Deans & Dixon, 1992; Muzzarelli, 1977, 1986; Peniche-Covas, Alvarez, & Arguelles-Monal, 1992; Udaybhaskar, 1990). The adsorption of Cu^{2+} , Hg^{2+} , Ni^{2+} and Zn^{2+} on chitosan with various particle sizes (210–1000 μM) and as a function of temperature was studied at neutral pH by McKay, Blair and Findon (1989). Particle size does not have any great influence on saturation adsorption capacity and an increase in temperature decreases the saturation adsorption capacity of chitosan. The saturation adsorption capacities for Cu^{2+} , Hg^{2+} , Ni^{2+} , Zn^{2+} on chitosan particles of 700–1000 μM were found to be 222, 815, 75 and 164 mg/g, respectively. Chitosan has also been effectively used for removal of Hg^{2+} from hard waters at neutral pH (Muzzarelli & Rocchetti, 1974) and arsenic concentration in ground water can be lowered to <0.05 ppm (Elson, Davies, & Hayes, 1980).

2. Chitosan derivatives as metal binding agents

2.1. Crosslinked chitosans

Partial crosslinking of chitosan by di/polyfunctional reagents is generally carried out to enable it to be used for metal complexation in acidic medium. The adsorption capacity depends on the extent of crosslinking and generally decreases with increase in extent of crosslinking. Further crosslinking in homogenous condition leads to enhanced metal binding capacity as a result of increased hydrophilicity caused by partial destruction of crystallinity, as compared to heterogeneous crosslinking. It was found that the binding capacity of chitosan for copper increased from 74 to 96% when it was crosslinked by glutaraldehyde in homogenous conditions with aldehyde–amine ratio 0.7. Increasing the aldehyde–amine ratio beyond 0.7 led to decreased binding capacity (Koyama & Taniguchi, 1986). The same effect was observed by introducing long chain alkyl groups like nonanoyl into chitosan (Kurita, Koyama, & Taniguchi, 1988). When chitosan beads were cross-linked with glutaraldehyde under heterogeneous conditions, it was found that the saturation adsorption capacity of Cd^{2+} on crosslinked chitosan decreased exponentially from 250 to 100 mg/g as the extent of crosslinking increased from 0 to 1.3 mol glutaraldehyde/mol of amine (Hsien & Rorrer, 1997). This is because of the restricted diffusion of molecules through the polymer network and reduced polymer chain flexibility (Ruiz,

Sastre, Maria, & Guibal, 2000). Also, the loss of amino binding sites by reaction with aldehyde is another major factor in this decrease.

Flake and powder forms of chitosan are not suitable for use as adsorbents due to their low surface area and non-porosity. They cause too great a pressure drop in an industrial scale column. This can be avoided by casting chitosan beads with high porosity and large surface area, together with crosslinking to make the beads insoluble in acidic media (Kawamura, Mitsuhashi, Tanibe, & Yoshida, 1993; Rorrer, Hsien, & Way, 1993).

Glutaraldehyde crosslinking has been used for Cd^{2+} recovery from industrial waste streams on porous magnetic chitosan beads of different diameters. The saturation adsorption capacity for Cd^{2+} on beads of 1 mm diameter was 518 mg/g of beads (Rorrer et al., 1993). Molybdenum and vanadium sorption on glutaraldehyde crosslinked chitosan has been studied by Guibal and Milot (1998).

Besides glutaraldehyde, many other crosslinking agents have been used such as epichlorohydrin (Baba, Hirakawa, & Kawano, 1994), ethylene glycol diglycidyl ether, iminodiacetic acid (Shim & Ryu, 1998), nitriloacetic acid, organic diisocyanates, etc. (Tikhonov, Radignina, & Yamskov, 1996). Chitosan crosslinked with ethylene glycol diglycidyl ether, diethylene glycol diglycidyl ether and polyethylene glycol diglycidyl ether had good selectivity for Cu^{2+} over Ni^{2+} and Co^{2+} (Qu & Lui, 1996,a,b,c). Good adsorbents for heavy metals such as Hg^{2+} and Cd^{2+} can be obtained by crosslinking chitosan with organic diisocyanates such as hexamethylene diisocyanate (Tokura & Seo, 1986), and nitriloacetic acid (Tikhonov et al., 1996).

2.2. Effect of templated chitosans

Earlier attempts to overcome the problem of decreased adsorption capacity of crosslinked chitosans led to a new chitosan derivative, viz. ‘crosslinked metal complexed chitosan’ (Ohga, Kurauchi, & Yanase, 1987). Metal complexed chitosans were synthesized by using a metal cation as template; crosslinking and then removing the templated ion akin to molecularly imprinted systems. The resins had high selectivity and their adsorption capacities were dependent on pH. The metal ion, which was used as a template, showed maximum adsorption. Also the resins were quite stable in acidic medium and could be reused. It was observed that the resins obtained by crosslinking chitosan with chloromethyl oxirane and template ions such as Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Fe^{3+} had higher abilities to adsorb Cu^{2+} than a resin obtained from chitosan in absence of metal ion. Resins from Cd^{2+} chitosan complex could act as effective adsorbents for Hg^{2+} . It was concluded that a selective separation of Cu^{2+} , Hg^{2+} and Cd^{2+} could be affected by using an appropriate resin obtainable from Cd^{2+} complexed chitosan.

In a study of the adsorption behavior of crosslinked Cu^{2+} complexed chitosan (i.e. Cu^{2+} as template ion in

the crosslinked chitosan) towards Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Fe^{3+} , Pb^{2+} , Co^{2+} , Ag^{2+} , Mo^{4+} , V^{5+} , In^{3+} , Ga^{3+} , Al^{3+} , from ammonium nitrate solution (Inoue, Baba, & Yoshizuka, 1993), although the amount of adsorption decreased for metal ions as compared to chitosan, the selectivity was greatly increased as compared to commercial iminodiacetic acid type chelating resin, viz. Lewatit TP-207. It was easier to separate Cu^{2+} selectively over other divalent metal ions. Mutual separation between ion pairs, e.g. Ni^{2+} over Co^{2+} and Fe^{3+} over other trivalent metals was achieved, which was poor in case of commercial chelating resin. It was confirmed that Cu^{2+} is selectively adsorbed on the above-mentioned resin having Cu^{2+} as template ion and that the adsorption was maximum at pH 5–6 (Haung, Han, Li, Yin, & He, 1998). When a similar crosslinked chitosan resin had Ni^{2+} as a template ion, it was found to have good adsorption capacity for Ni^{2+} and Co^{2+} . The capacity was 5–6 times higher in case of Ni^{2+} and two times higher in case of Co^{2+} , than non-templated resin (Qu & Lui, 1996a,b,c).

The adsorption from dilute HCl solution of Pt^{4+} and Pd^{2+} onto crosslinked copper complexed chitosan took place by anion exchange mechanism and both the metal ions were adsorbed as ion pairs while Cu^{2+} was adsorbed as a chelate coordinated by amino and hydroxyl groups of chitosan (Inoue et al., 1993).

A resin synthesized by reacting chitosan with 5-chloromethyl 8-quinolinol hydrochloride has been cross-linked by a template crosslinking method with Ga^{3+} as template. Ga^{3+} was templated on this oxine type chemically modified chitosan (Fig. 1) (Inoue et al., 1996a,b). In a comparison of the adsorption capacities of this resin for Mo^{4+} , V^{4+} , In^{3+} , Al^{3+} , Zn^{2+} , Fe^{2+} , Cd^{2+} and Ga^{3+} from dilute H_2SO_4 solution with those for chitosan, the adsorption took place on the templated resin at a pH much lower than chitosan and the shift was greatest for Ga^{3+} . Also, selective separation of Ga^{3+} and In^{3+} from a large excess of Zn^{2+} was achieved. The maximum adsorption capacity was 1.17 mol/kg of dry resin. A resin synthesized by crosslinking chitosan with glutaraldehyde and with Zn^{2+} as template (Haung, Yuan, & Wang, 2000) showed considerable adsorption capacity for Zn^{2+} , Cd^{2+} , Hg^{2+} and was stable under acidic conditions.

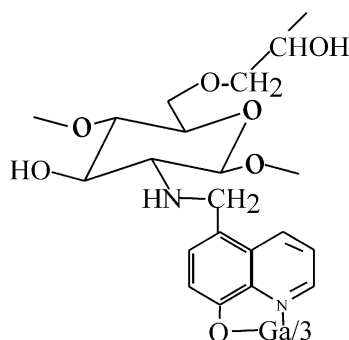


Fig. 1. Ga templated oxine chitosan.

2.3. Derivatives of chitosan containing Nitrogen as heteroatom

2.3.1. Amino acid glucans

The reaction of chitosan with aldehydo acids followed by reduction gives derivatives called amino acid glucans. For example, reaction of chitosan with glyoxylic acid followed by reduction with sodium borohydride gives *N*-carboxymethyl chitosan, which is called glycine glucan (Fig. 2). The derivative is water-soluble and can form insoluble metal chelates after addition to transition metal ion solutions. It has good adsorption capacity for Cu^{2+} , Ni^{2+} , Zn^{2+} , Hg^{2+} , Pb^{2+} , Co^{2+} , Cd^{2+} , UO^{2+} at neutral pH (Muzzarelli & Tanfani, 1982). As incorporation of glycine residues onto chitosan reduces the conformational rigidity of the polymer, it shows higher adsorption for metal ions than chitosan and fully deacetylated chitosan even though the latter has more free amino groups (Delben, Muzzarelli, & Terbojevich, 1989). The order of affinity for divalent metal ions was found to be $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$, $\text{Ni}^{2+} > \text{Co}^{2+}$ (Muzzarelli & Delben, 1992). The binding capacities were affected by charge density, temperature and pH. The involvement of *N*-carboxymethyl residues in the chelation process was confirmed since the binding constants were affected by the density of glycine residues (Dobetti & Delben, 1992). Glycine glucan could effectively remove Co^{2+} and Cu^{2+} from sodium fluoride and sodium chloride brines (Muzzarelli, 1985). The crosslinked glycine glucan showed much higher capacity for Cu^{2+} uptake than chitosan. It was also effective in adsorbing Co^{2+} from dilute solutions, unlike chitosan (Muzzarelli, 1983a,b; Muzzarelli & Tanfani, 1985). Aspartate glucan and serine glucan were similarly synthesized by reacting chitosan with oxaloacetic acid and β -hydroxy-pyruvic acid (Muzzarelli & Tanfani, 1985). The derivatives had much higher adsorption capacities for transition metals, especially Co^{2+} and Cu^{2+} , than chitosan.

A polyampholyte, *N*-(*O*-carboxybenzyl) chitosan, similar to *N*-carboxymethyl chitosan prepared by reaction of chitosan with phthalaldehydic acid in presence of a reducing agent was also water soluble and formed insoluble metal chelates with pH dependent yields. In the polymer concentration range studied (200–500 mg/ml), Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} and UO^{2+} could be removed from dilute solutions and complete removal of Cu^{2+} and Pb^{2+} even at higher concentration was achievable (Muzzarelli & Tanfani, 1982).

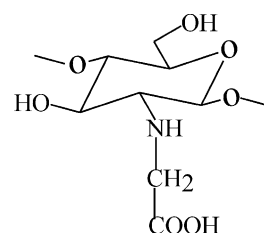


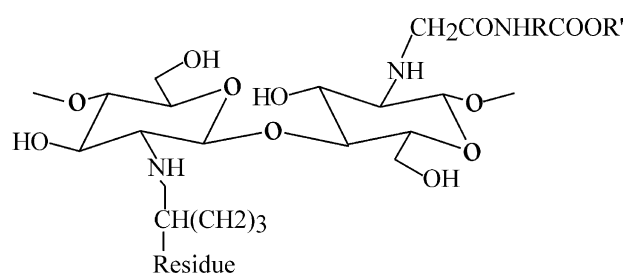
Fig. 2. *N*-carboxymethyl chitosan/glycine glucan.

In a study of the chelation of Zn^{2+} with an *N*-*O*-carboxymethyl derivative of chitosan and the dependence of formation of complex on temperature, ionic concentration, ligand concentration (Hon David & Tang, 2000), the favorable conditions for Zn^{2+} chelate formation were at the lower Zn^{2+} ionic concentration (0.005 M), temperature 50 °C and ligand concentration of 0.5 g/200 ml ZnSO_4 . Further study of association complex between Zn^{2+} and *N*-*O*-carboxymethyl chitosan revealed that the hydroxyl and amino groups do not participate in the formation of complex. The chelation sites occurred at carboxyl groups as suggested by IR spectra. Also, it was found that the water insoluble chelates had tetrahedral structures. Water-soluble derivatives were formed as a consequence of electrostatic attraction and Zn^{2+} was bound to the oxygen of the carbonyl group and water. Amino acid glucans therefore can be used to remove transition metal ions from dilute solutions as well as brines. The derivatives unlike chitosan can be used to remove Co^{2+} quantitatively. They can be effectively used under acidic conditions and in chloride and fluoride brines.

2.3.2. Amino acid conjugates of chitosan

Amino acid conjugates of chitosan, synthesized by reacting chitosan/partially crosslinked chitosan with esters of amino acids (Fig. 3). Adsorption of Co^{2+} and Mn^{2+} was increased dramatically after substitution of amino acids onto chitosan (see Table 1) (Hiroshi, Malko, Boonma, & Tomoyo, 1995).

Tests of the adsorption capacities of glutaraldehyde crosslinked chitosan derivatised with *N*-methyl glycine, *N*-acetyl glycine (Becker, Schlaak, & Strasdeit, 2000) for Cd^{2+} , Ni^{2+} and Zn^{2+} from chloride, nitrate and sulphate solutions demonstrated the the capacities were equivalent to those for glutaraldehyde crosslinked chitosans. Study of the counter ion effect revealed that the Cd^{2+} had maximum adsorption from chloride solutions and it was adsorbed as an anionic chloro complex. Hence amino acid conjugates of chitosan can be used effectively for removal of Mn^{2+} and Cd^{2+} .



Residue-Glutaraldehyde Crosslinked Chitosan

R-side chain of amino acid

R'- alcohol component of the ester

Fig. 3. Chitosan–amino acid conjugate.

Table 1

Extent of percentage removal of heavy metals by chitosan and modified chitosan for single ion solution (initial concentration 100 ppm) (Hiroshi et al., 1995)

Adsorbent	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}
Chitosan	98.3	78.5	21.0	7.0
Glycine–chitosan	58.0	31.5	17.0	28.0
Alanine–chitosan	99.7	100	100	100
Serine–chitosan	99.8	100	100	100
Leucine–chitosan	99.5	100	99.9	100

2.3.3. Pyridyl methyl chitosans

Reaction of 2-pyridine carbaldehyde with chitosan produced the corresponding arylidine derivative, which was crosslinked prior to borohydride reduction (Fig. 4). The derivative was selective for Pd^{2+} over base metals in low pH range and for Cu^{2+} over iron in aqueous ammonium nitrate solutions (Baba, Masaaki, & Kawano, 1995; Inoue, Ohto, Yoshizuka, Yamaguchi, & Tanaka, 1997). While further exploring the behavior of pyridyl methyl chitosan (PMC), it was found that the derivative selectively adsorbed Ni^{2+} and Pd^{2+} , which formed planar complexes at a lower pH compared to crosslinked chitosan (Baba, Masaaki, & Kawano, 1998a; Baba, Matsumara, Shiomori, Kawano, 1998b). The metal ions, which form octahedral complexes such as Cd^{2+} , Zn^{2+} , Co^{2+} , were adsorbed at almost the same pH range as crosslinked chitosan, and Hg^{2+} could be selectively adsorbed on pyridyl methyl chitosan from dilute HCl solution (Baba et al., 1998a,b).

N-(2-Pyridyl methyl) and *N*-(4-pyridyl methyl) derivatives of chitosan with the same degrees of substitution have been synthesized, and the equilibrium constants of adsorption of Cu^{2+} in aqueous solutions (Rodrigues, Laranjeira, De, Valfredo, & Sadler, 1998) were higher for *N*-(2-pyridyl methyl) chitosan and the difference in values was attributed to the position of substitution of the pyridine ring. Pyridyl methyl chitosan therefore is good for adsorption of transition metals which form planar complexes, e.g. Ni^{2+} , Pd^{2+} , Cu^{2+} , Hg^{2+} , etc.

2.3.4. Chitosan–pyridoxal

Chitosan–pyridoxal was synthesized by reacting chitosan and pyridoxal hydrochloride and then reducing the product formed with sodium cyanoborohydride (Fig. 5) (Lasko, Pesic, & Oliver, 1993). The derivative showed

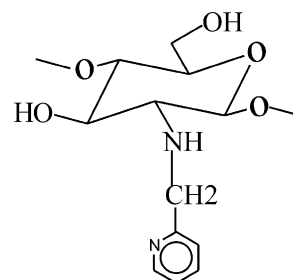


Fig. 4. 2-Pyridyl methyl chitosan.

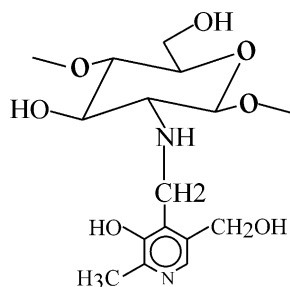


Fig. 5. Chitosan–pyridoxal.

enhanced adsorption capacities for Cu^{2+} , Pb^{2+} and Fe^{3+} than chitosan.

The derivative could adsorb 71% of the copper from 100-ppm solution at pH 5 in 2 h as compared to 54% by chitosan under identical conditions.

The derivative was found to have the highest adsorption capacity for copper as compared to other derivatives synthesized, viz. chitosan mercaptosuccinate, thiirane chitosan and succinamide chitosan. When the derivative was crosslinked with epichlorohydrin, the derivative was selective for copper over iron, zinc and cadmium; the adsorption being pH dependent and increase in pH from 2.5 to 6 increased the Cu^{2+} adsorption. No iron was adsorbed on the polymer (Pescic, Oliver, Raman, & Lasko, 1994, 1998). The derivative, *N*-(2-hydroxy-3-methyl aminopropyl) chitosan, had better adsorption capacities for Cu^{2+} and Hg^{2+} than starting chitosan (Table 2) (Cardenas, Orlando, & Edolio, 2000). Nitrogen containing derivatives were found to be good for adsorption of copper and mercury.

2.4. Derivatives of chitosan containing phosphorus as heteroatom

2.4.1. Phosphorylated chitosans

Phosphorylation of chitosan and chitin has been achieved using urea and orthophosphoric acid in dimethylformamide. The adsorption of uranium was found to be much greater than Cu^{2+} , Cd^{2+} , Mn^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , mg^{2+} , Ca^{2+} and was pH dependent. It was also sensitive to temperature, granule radius and the co-existence of carbonate ion. Low concentrations of carbonate ions (0–0.3 mM) did not affect the adsorption of uranium greatly. However, increase in the concentration of carbonate ions from 0.5 to 3 mM decreased the adsorption of uranium from approximately 40 mg of U/g of adsorbent to values tending to zero. The adsorption was

also dependent on the concentration of external uranium solution and increased linearly with increase in concentration of uranium. The adsorption was inversely proportional to the amount of adsorbent used (Sakasguchi, Horikoshi, & Nakajima, 1981).

Phosphorylation was also achieved by reaction with phosphorus pentoxide in methanesulphonic acid (Nishi et al., 1986). Fully substituted derivatives were obtained and it was found that the compounds with high degrees of substitution were insoluble in water. The derivatives had high binding capacity for Cu^{2+} and one Cu^{2+} was bound to two phosphated glucosamine residues. Phosphorylation of epichlorohydrin crosslinked chitosan by tri-methyl phosphate– POCl_3 and H_3PO_4 –DMF reactions improved metal binding ability of chitosan when concentration of metal solution was high (Yoo & Lee, 1997). Chitosan–tripolyphosphate–chelating resin was prepared by an ionotropic crosslinking method which gave crosslinked acid resistant chitosan beads in one step by avoiding prior coagulation and then crosslinking. Also, the use of environmentally hazardous reagents such as glutaraldehyde, ethylene glycol diglycidyl ether was avoided. The process involved formation of crosslinked chitosan beads by dropping chitosan solution in the solution of sodium tripolyphosphate. It was observed that the ionotropic crosslinking method resulted in reduction of crystallinity and amino binding sites for metal ions. As a consequence Cu^{2+} uptake decreased. The adsorption capacity was found to be a function of ionic crosslinking density and pH. Higher crosslinking densities decreased the adsorption capacities. At low pH (pH 2–3) no significant binding observed. The saturation adsorption capacity for Cu^{2+} ion occurred at pH 5 and the highest adsorption capacity of chitosan–tripolyphosphate beads was 200 mg/ g of beads at an initial concentration of 1000-ppm Cu^{2+} . The mechanism of adsorption was chelation rather than ion exchange (Lee, Mi, Shen, & Shyu, 2000). The derivatives containing phosphorus as heteroatom improved the binding capacities of chitosan and chitin for copper and mercury and was also good in adsorbing UO_2^{2+} .

2.5. Derivatives of chitosan containing Sulphur as heteroatom: dithiocarbamate chitosan

Dithiocarbamate chitosan (DTCC) prepared by reacting chitosan with carbon disulphide (Fig. 6) (Muzzarelli

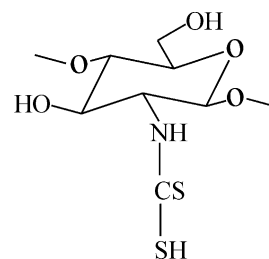


Fig. 6. Dithiocarbamate chitosan.

Table 2
Isotherm parameters for mercury and copper (Cardenas, Orlando, Edolio, 2000)

Parameter for polymers	pH	Hg Q_{max} (mg/g)	Cu Q_{max} (mg/g)
Chitosan	2.5	357	135
	4.5	454	238
Derivative	2.5	556	208
	4.5	588	238

& Tanfani, 1982), is a water insoluble derivative effective in adsorbing Cu^{2+} , Ni^{2+} , Co^{2+} and Cd^{2+} from 0.5-mmol/l solution at low pH (2–3). Zn^{2+} , Hg^{2+} , Ag^+ , Pd^{2+} , UO^{2+} were adsorbed totally at pH 5–7. The adsorption capacity of Co^{2+} and Cd^{2+} were largely different from those of dithiocarbamatecellulose (Imai, Muroi, Hamaguchi, Matsushita, & Koyama, 1980).

Dithiocarbamate type chemically modified chitosan may also be prepared by incorporating functional groups of dithiocarbamate onto chitosan (Asakawa, Inoue, Katsutoshi, & Tanaka, 2000). The derivative is selective for Ag^+ , Au^{3+} and Pd^{2+} with maximum adsorption capacity for Ag^+ being 3.6 mol/kg. It has higher adsorption capacities than chitosan and chelating resins containing the same functional groups. A sulphonated derivative of chitosan, prepared by reacting chitosan with chlorohydrin or epoxy compounds containing an SO_3 group, contained 8% S and readily complexed with Fe (Butelman, 1990). Chitosan *N*-benzyl mono- and disulphonates are good sorbents for removal of metal ions in acidic media (Weltowski, Martel, & Morcellet, 1996). The derivatives may be synthesized by reacting chitosan with 2-formyl benzene sodium sulphonate and 4-formyl-1,3-benzene sodium disulphonate followed by reduction with sodium cyanoborohydride. The adsorption properties for Cd^{2+} , Zn^{2+} , Ni^{2+} , Pb^{2+} , Cu^{2+} , Fe^{3+} and Cr^{3+} are higher in the case of disulphonate derivative than the monosulphonate derivative. The monosulphonate derivatives could only bind 7% of Cr^{3+} in 5 ppm solution while the disulphonate derivative could bind 25 and 26% of Fe^{3+} and Cr^{3+} from 5 ppm solutions, respectively. The disulfonate derivative was especially effective in the lower pH range of 2–4. It was shown that the amphoteric character of monosulphonated derivative was unfavorable for the sorption because of the intramolecular interaction occurring between amino and sulphonate group (Fig. 7). Protection of the amino groups of chitosan by benzyloxycarbonyl successfully improved its adsorption capacity by reducing the intramolecular interactions between amino and sulphonate groups. The protected monosulphonated derivatives had higher adsorption capacities than disulphonated derivatives. Thus, protected monosulphonated

derivatives could bind 37 and 45% of Fe^{3+} and Cr^{3+} from 5-ppm solutions, respectively.

A thiosemicarbazide derivative of chitosan, prepared by the reaction of chitosan with ammonium thiocyanate and hydrazine, was insoluble in all organic solvents was considered to have crosslinked network structure (Choi, 1990). It was found to be good adsorbent for Hg^{2+} and the order of adsorptivity was found to be $\text{Hg}^{2+} > \text{UO}^{2+} > \text{Cu}^{2+}$. *N*-thiocarbamoyl chitosan derivatives prepared by reaction of chitosan with isothiocyanate compounds showed good adsorption for metals such as Cu^{2+} (Hayasaka, Takano, & Satake, 1996).

The derivatives of crosslinked chitosan like thienyl methyl and methyl thio modified chitosans showed high selectivities for Au^{3+} , Pd^{2+} , Pt^{4+} (Baba & Inoue, 1997) and Hg^{2+} (Baba et al., 1998a,b) over base metals in hydrochloric acid solution. The degree of adsorption of Pd^{2+} on the derivative was a function of chloride ion concentration. It was found that the adsorption capacities of these derivatives for Pd^{2+} were 2.5–3 times greater than for 2-chloromethyl oxirane chitosan and commercial chelating resins (Baba, Kawano, & Hirakawa, 1996). The adsorption properties of the chelating resins obtained by crosslinking of chitosan chloromethyl thiirane were dependent on sulphur content and increase in the adsorption capacities for noble metals such as Ag^{2+} , Au^{3+} , Pd^{2+} , Pt^{4+} was observed with increased sulphur content. The resins containing 24% sulphur were found to possess adsorption capacities of 4.46, 4.86, 3.14 and 1.87 mmol/g for Ag^+ , Au^{3+} , Pd^{2+} and Pt^{4+} , respectively (Xu & Ni, 1991).

Derivatives of chitosan with mercaptosuccinic acid and thiirane have been synthesized in order to decrease the binding capacity of chitosan for iron. Thereby the binding capacity of chitosan–mercaptosuccinic acid was improved two fold for Cd^{2+} and five fold for Pb^{2+} as compared to chitosan but the derivative bound negligible iron. Chitosan thiirane bound three times as much Pb^{2+} as compared to chitosan (Lasko et al., 1993). Ester derivatives with (R) thiazolidine-4-carboxylic acid and with thioglycolic acid of crosslinked chitosan had good selectivities over the pH range 3–6 for Ni^{2+} and Cd^{2+} over Zn^{2+} , mg^{2+} and Ca^{2+} (Becker et al., 2000). Considerable adsorption even at low pH was explained by the formation of stable metal chelates between metal ions and the functional groups 1,3-diaminopropane tetracetic acid and thioglycolic acid. A thiourea derivative was found to have good adsorption properties for Pd^{2+} and Pt^{4+} , was selective for Pd^{2+} over Pt^{4+} , and its maximum adsorption capacities were less affected by the presence of competitor anion, especially sulphate. (386.9 mg/g of derivative obtained for Pt^{4+}) (Guibal, Vincent, & Mendoza, 2000). A methyl thiourea derivative of chitosan exhibited a high selectivity for precious metals such as Ag^+ , Au^{3+} , Pd^{2+} and Pt^{4+} over base metals (Baba, Noma, & Hoaki, 1999).

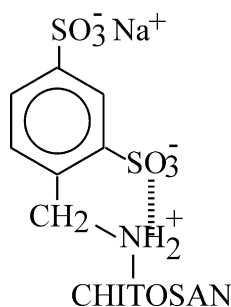
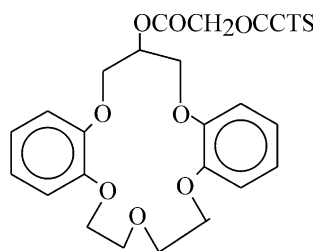


Fig. 7. Intramolecular interactions between amino group of chitosan and sulphonate groups.



CCTS-crosslinked chitosan

Fig. 8. CCTS-1.

2.6. Other derivatives of chitosan

2.6.1. Chitosan crown ethers

Crown ether derivatives like Dibenzo-16-Crown-5-acetate crown ether (CCTS-1) (Fig. 8) and 3,5 di-tert.butyl dibenzo-14-Crown-4 diacetate crown ether (CCTS-2) (Fig. 9) derivative of crosslinked chitosan showed good adsorption selectivities for Pb^{2+} over Cu^{2+} and Cr^{3+} (Tan, Wang, Peng, & Tang, 1999). The values are given in Table 3.

It was also found that for aqueous system containing Pb^{2+} and Ni^{2+} or Cu^{2+} and Ni^{2+} CCTS-1 adsorbed only Pb^{2+} or Cu^{2+} . Also CCTS-2 adsorbed selectively Pb^{2+} from aqueous system containing Pb^{2+} , Cr^{3+} and Ni^{2+} . The adsorption properties were dependent on acidity of the medium and it was observed that in case of Cu^{2+} lowering the pH below 3 reduced the adsorption capacity drastically. The limit was pH-2 for Pb^{2+} . For Cr^{3+} the adsorption rate was >99% in the 2–6 pH range.

Schiff's base type crosslinked chitosan crown ethers (CCTSN=CH-B-15-C-5) (Fig. 10) and (CCTSN=CH-B-18-C-6) (Fig. 11), synthesized by reaction of crosslinked chitosan with 4'-formyl benzo 15-Crown-5 and 4'-formyl benzo-18-Crown-6, had lower metal ion adsorption capacities than does chitosan, but they were more selective for Ag^+ and Pd^{2+} . The derivatives had good adsorption and selectivity properties for Pd^{2+} with the coexistence of Pb^{2+} and Cr^{3+} . CCTSN=CH-B-15-C-5 could adsorb 38.7 mg/g Pd^{2+} , 3.9 mg/g of Pb^{2+} and no Cr^{3+} . CCTSN=CH-B-18-C-6 could bind 36.8 mg/g of Pd^{2+} , 3.2 mg/g of Pb^{2+} and no Cr^{3+} . CCTSN=CH-B-15-C-5 was found to be selective for Ag^+ over Pb^{2+} at pH 6, the capacity being 52.5 mg/g for Ag^+ and 4.1 mg/g for

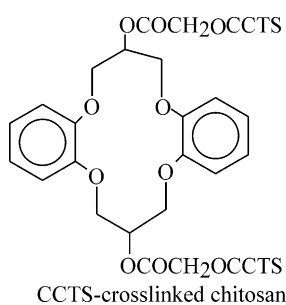


Fig. 9. CCTS-2.

Table 3

Adsorption capacities of crown ether derivatives of chitosan for metal ions (mg metal ions/g adsorbent) at pH 5.6

Metal ion	Pb^{2+}	Cu^{2+}	Cr^{3+}
CCTS-1	29.1	23.9	17.3
CCTS-2	60.2	31.3	30.5
CCTS	24.0	16.8	18.6

Pb^{2+} . Also, CCTSN=CH-B-15-C-5 (52.5 mg/g) had a greater adsorption capacity for Ag^+ than CCTSN=CH-B-18-C-6 (28.2 mg/g). This was attributed to the smaller radius of the crown ether CCTSN=CH-B-15-C-5 than the CCTSN=CH-B-18-C-6 (Peng, Wang, & Tang, 1998).

Aza crown ether grafted chitosan and mesocyclic diamine grafted chitosan crown ether showed high selectivity for Cu^{2+} in presence of Pb^{2+} and Cd^{2+} (Yang, Wang, & Tang, 1999, 2000). *N*-schiff base type chitosan crown ethers and *N* secondary amine type chitosan crown ether showed good adsorption selectivity for Pd^{2+} in the presence of Cu^{2+} and Hg^{2+} . Chitosan modified by 3'-allylbenzo15-C-5 and 4'-allylbenzo15-C-5 had good adsorption capacity and selectivity for Pd^{2+} in the presence of Cu^{2+} and Hg^{2+} (Wang, Tan, Peng, Tang, & Luan, 1999).

2.6.2. Chitosan EDTA/DTPA complexes

Complexone type modified chitosans have been synthesised by reacting chitosan with ethylene diamine tetraacetic acid (EDTA) anhydride and diethylenetriamine-pentaacetic acid (DTPA) anhydride (Figs. 12 and 13). A comparative study of glycine–chitosan, iminodiacetic acid–chitosan, EDTA–chitosan and DTPA–chitosan showed that mutual separation between adjacent rare earth metals was possible by using chitosan–EDTA/ DTPA complexes. Also, adsorption of metals took place at a much lower pH than for chitosan (Inoue et al., 1996a,b). The chitosan EDTA conjugate could bind 2 mmol of Zn^{2+} /g of polymer at pH 6.5 (Bernkop, Schnurch, Paikl, & Valenta, 1997). Chitosan–EDTA/DTPA complexes have high selectivity for Pb^{2+} over Zn^{2+} at low pH and the adsorption capacities are independent of the counterions such as chloride and nitrate. The dried gel of chitosan–EDTA, DTPA complex could bind 1.5 and 1.8 mol Pb^{2+} /kg (Inoue et al., 1997). The order of adsorption from sulphuric acid solution for base metals was $\text{Ga}^{3+} = \text{In}^{3+} = \text{Fe}^{3+} = \text{Cu}^{2+} = \text{Mo}^{4+} > \text{Ni}^{2+} > \text{V}^{4+} > \text{Zn}^{2+}$, $\text{Co}^{2+} > \text{Al}^{3+} \gg \text{Mn}^{2+}$. Separation

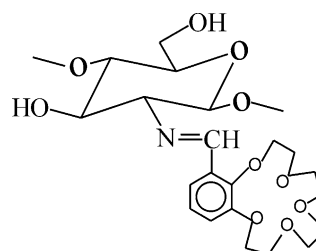


Fig. 10. CCTSN=CH-B-15-C-5.

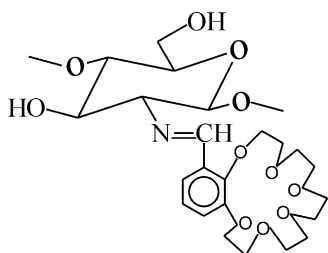


Fig. 11. CCTSN=CH-B-18-C-6.

between Ni^{2+} and Co^{2+} as well as recovery of small amounts of Ni^{2+} and Co^{2+} from large excess of Al^{3+} could be achieved. It was also observed that the pH at which adsorption takes place was much lowered as compared to chitosan, e.g. Cu^{2+} was adsorbed on the conjugate at pH 1 whereas on chitosan it was adsorbed at pH 4–6. The chitosan–EDTA/DTPA conjugates were found to be useful for separation of adjacent rare earth metals which is not achievable with commercial chelating resins.

2.6.3. Chitosan graft copolymers

A polyaminated highly porous resin has been prepared from porous beads of chitosan by crosslinking with ethylene glycol diglycidyl ether and then reacting the crosslinked beads with epichlorohydrin and polyethyleneimine, respectively (Fig. 14).

The order of selectivity of adsorption of metal ions onto the resin at pH 7. was $\text{Hg}^{2+} > \text{UO}_2^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$. mg^{2+} , while Ca^{2+} , Ga^{3+} , As^{3+} , Sr^{2+} were not adsorbed on the resin at all. The selectivity depended on the pH, with the amount of metal adsorbed decreasing with decrease in pH. The resin was found to have higher adsorption as compared to commercial chelate resin (Kawamura et al., 1993). The mechanism of adsorption was shown to be pore diffusion as well as surface diffusion in polyethyleneimine–chitosan particles (Kawamura, Yoshida, Asai, & Tanibe, 1997). The resin could be effectively reused after repeated cycles of adsorption and elution. Elution of Hg was effected by sulphuric acid (Kawamura, Yoshida, Asai, & Tanibe, 1998).

Chitosan grafted with polyacrylonitrile has been further derivatised to yield amidoximated chitosan (Fig. 15) (Kang, Choi, & Kweon, 1996), a derivative has higher adsorption

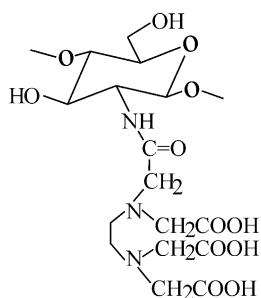


Fig. 12. EDTA chitosan.

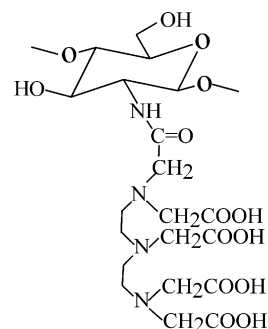


Fig. 13. DTPA chitosan.

for Cu^{2+} , Mn^{2+} and Pb^{2+} compared to crosslinked chitosan. The adsorption capacity had a linear dependence on pH in cases of Cu^{2+} and Pb^{2+} . However, a slight decrease in the adsorption capacity was observed in case of Zn^{2+} and Cd^{2+} (Kang, Choi, & Kweon, 1999).

Chitosan-graft-polyvinyl pyrrolidone, synthesized by homogenous grafting of vinyl pyrrolidone onto chitosan (Yazdani & Retuert, 1997), was insoluble in common organic solvents and organic/inorganic acids. It could effectively bind Cu^{2+} and then became soluble in dilute hydrochloric acid. Amphoteric flocculents, which can function as polycationic flocculents in acidic media and polyanionic flocculents in basic media, having much higher adsorption properties were synthesized by grafting alkanedioic, alkenedioic as well as alkenoic acids (Kim, 1997; Kim, Han, Yun, & Kang, 1998).

2.6.4. Chitosan graft sugars

Chitosans modified with different mono as well as disaccharides constitute this class of derivatives. Deoxy-lactit-1-yl-chitosan could form complexes with Cu^{2+} and Fe^{3+} (Chiessi, Palleschi, Paradossi, Venanzi, & Pispisa, 1991). D-galactose modified chitosan adsorbed rare earth metals as well as base metals and the order of adsorptivity for trivalent metals was $\text{Ga}^{3+} > \text{In}^{3+} > \text{Nb}^{3+} > \text{Eu}^{3+}$ and for divalent metals it was $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$. The pH dependency on the distribution ratio was affected by valency of metal ion (Kondo, Sumi, & Matsumoto, 1996). Thus, chitosans with carbohydrate substituents are promising materials for further investigations.

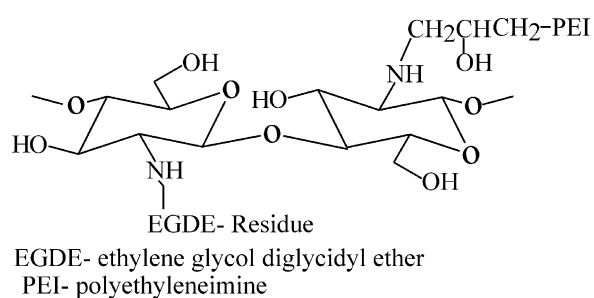


Fig. 14. Chitosan–polyethyleneimine complex.

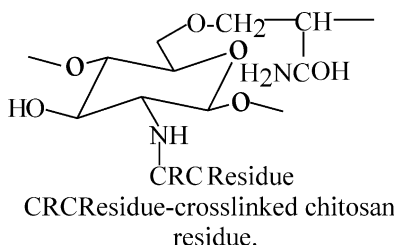


Fig. 15. Chitosan-g-polyacrylonitrile (amidoximated).

2.6.5. Chitosan derivatives with ketoacids

Chitosan derivatives with ketoacids were found effective in removal of Co^{60} from nuclear plant wastewaters as well as for uranium from dilute solutions and from saline waters (Muzzarelli, 1984, 1986).

It was shown that pyruvic acid modified chitosan (Fig. 16) had higher adsorption capacities for Cu^{2+} , Zn^{2+} , Co^{2+} than chitosan and salicylaldehyde modified chitosan (Ma, Zou, & Gao, 2000).

2.6.6. Chitosan derivatives with 1,3 dicarbonyl compounds

An amino-enone derivatives was obtained by reacting chitosan with dicarbonyl compounds such as 2,4-pentanedione. This derivative had 38 times higher chelating capacity for Cu^{2+} and Co^{2+} than chitosan, and was stable in the pH range 3–9 (Gomez-Guillen, Gomez-Sanchez, & Martin-Zamora, 1992, 1994).

2.6.7. Chitosan–cyclodextrin conjugates

Networks based on chitosan and β -cyclodextrin were prepared by reacting chitosan with oxidized cyclodextrin. Stability and structural characteristics of the Cu^{2+} complex as a catalyst during the oxidation of adrenaline were studied and it was found that the structural and catalytic features of Cu^{2+} bound to matrix were retained (Paradossi, Chiessi, Cavalieri, Moscone, & Crescenzi, 1998).

2.6.8. Halogenated derivatives

N-Halochitosans prepared by reacting chitosan with sodium hypochlorite are good flocculents for metallic oxides along with many other contaminants (Dingilian & Heinsohn, 1992). *N*-chloroacetyl chitosan, prepared by reacting chitosan with chloroacetic anhydride in chloroacetic acid exhibited high affinity for cations such as Cu^{2+} , Fe^{3+} (Mori, Mori, Nishiyama, & Kurita, 1999).

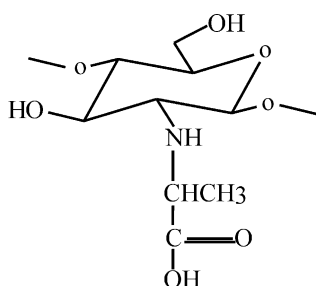


Fig. 16. Pyruvate chitosan.

2.7. Methods of analysis of the metal complexes

2.7.1. Determination metal bound to chitosan derivatives

2.7.1.1. Indirect determination. The amount metal adsorbed on the polymer can be determined by equilibrating the polymer in a metal ion solution of known concentration, followed by determination of the amount of metal ion in the supernatant by atomic absorption spectroscopy, (AAS) (Baba et al., 1996; Hiroshi et al., 1995; Kawamura et al., 1997; Kondo et al., 1996; Lasko et al., 1993; Weltowski et al., 1996), titration with EDTA (Inoue et al., 1993), UV spectra (Muzzarelli & Tanfani, 1982), etc.

2.7.1.2. Direct determination. The metal ion bound to the polymer can be determined by decomposing the polymer–metal complex in concentrated nitric acid and then measuring the concentration by AAS (Becker et al., 2000).

2.8. Determination of sorption mechanism, structure of complex by SEM, EDAX, XPS, IR, ^{13}C NMR, DSC

2.8.1. SEM/ EDAX

Scanning electron microscopy (SEM) is an extremely useful method for visual confirmation of surface morphology and the physical state of the surface. SEM coupled with energy dispersive analysis of X-rays (EDAX) is used to determine the metal uptake mechanism on chitosan (Maruca, Suder, & Wightman, 1982) which is a complex phenomenon involving nodule formation on the polymer surface, ion adsorption and ion absorption. It may also be used to determine the porosity of chitosan beads as well as membranes and diffusion of metal ions through them. (Kim, Kim, Moon, & Yang, 1999).

2.8.2. XPS

X-ray photoelectron spectroscopy (XPS) is useful for determination of bonding energies of C, O and N on the surface of chitosan and its metal chelate (Ji, 2000), and is effective for determination of the coordination number of the chitosan metal complex, e.g. coordination number of chitosan- Ni^{2+} was found to be 6 and that of chitosan- La^{3+} was found to be 10 (Guan, Cheng, & Tong, 1999).

XPS also provided information regarding the forms of species absorbed on the polymer. For example, a study of interactions of Cu^{2+} , Mo^{4+} and Cr^{3+} with chitosan beads, crosslinked chitosan beads, and chitosan flakes has revealed that the adsorption of Mo^{4+} and Cr^{3+} on chitosan flakes and beads was followed by reduction of the Mo^{4+} and Cr^{3+} . Also it was clear that crosslinking allowed uniform distribution of the metals throughout the sorbent (Dambies et al., 2001).

2.8.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) is an effective tool in characterising chitosan and its metal chelates.

Table 4

Data on complexation of Cu, Co, Ni, Cd, Zn, Pb, Mn, Cr, Pd, Pt, Au, Ag, Hg, U, Ga and In ions

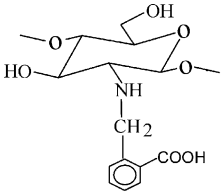
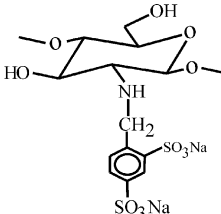
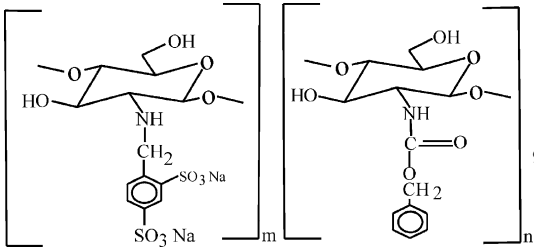
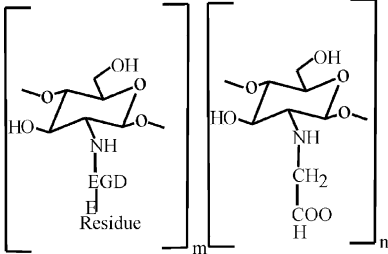
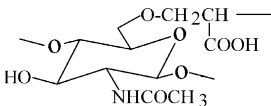
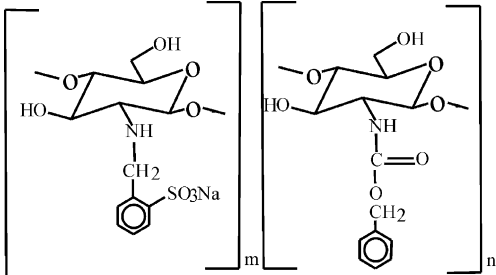
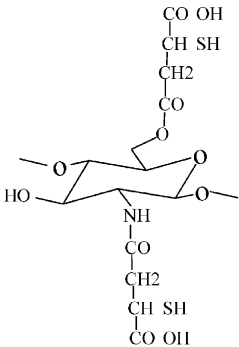
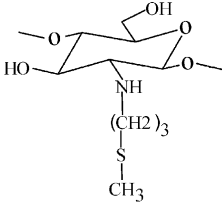
Metal	Structure of The Derivative	Binding Capacity	Remarks	Reference
Cu ²⁺	Fig. 6	90–100% from 0.5 mmol/l metal solution	Water insoluble derivative	Muzzarelli and Tanfani, 1982
	Fig. 2	100% Cu removed from 0.3 to 0.5 mmol/l metal solution	Water soluble derivative formed insoluble metal chelate	Muzzarelli and Tanfani, 1982
	 <p>N-carboxybenzyl chitosan</p>	100% Cu removed from 0.1 to 0.5 mmol/l metal solution.	Water soluble derivative formed insoluble metal chelate	Muzzarelli and Tanfani, 1982
O ²⁺	Fig. 14	99.9% removed from 100 ppm solution		Kawamura et al., 1993
	Fig. 6	100% from 0.5 mmol/l at pH 10–12 and decreases with decrease in pH		Muzzarelli and Tanfani, 1982
	Fig. 2	100% removal from 0.2 mmol/l		Muzzarelli and Tanfani, 1982
I ²⁺	Fig. 17	100% removal from 0.1 to 0.2 mmol/l.		Muzzarelli and Tanfani, 1982
	Fig. 16	Higher adsorption at pH 7 than chitosan salicylaldehyde–chitosan		Ma et al., 2000
	Fig. 3	99.9–100% from 100 ppm metal solution on 110 mg derivative		Hiroshi et al., 1995
	Fig. 14	66.7% removed from 100 ppm solution on 100 mg polymer at pH 7		Kawamura et al., 1993
	Fig. 6	100% removal from 0.5 mmol/l solution at pH 7–12 and decreases with decrease in pH		Muzzarelli and Tanfani, 1982.
	Fig. 2	100% removal from 0.2 mmol/l solution		Muzzarelli and Tanfani, 1982.
	Fig. 17	100% removal from 0.1 to 0.2 mmol/l solution		Muzzarelli and Tanfani, 1982
	Fig. 14	98.6% removal from 100 ppm solution		Kawamura et al., 1993
	 <p>Chitosan N-Benzyl disulphonate</p>	3% removal at pH 2	Can be used to remove metal ions from acidic water; high adsorption for Cr and Fe	Weltowski et al., 1996
	 <p>Chitosan N-benzyl disulphonate protected</p>	9% removal at pH 2	Can be used to remove metal ions from acidic water, high adsorption for Cr and Fe	Weltowski et al., 1996
	 <p>EGDE-ethylene glycol Residue-diglycidyl ether chitosan</p>		Higher capacity than chitosan	Muzzarelli, 1983
	Crosslinked N-carboxy methyl chitosan			

Table 4 (continued)

Metal	Structure of The Derivative	Binding Capacity	Remarks	Reference
Cd^{2+}	Fig. 16	99% from 100 ppm solution on 100 mg derivative		Kawamura et al., 1993
	 <p>Chitin graft Polyacrylonitrile Type1</p>	398 ppm on 1 g derivative at pH 5		Aly et al., 1997
	 <p>Chitosan N-benzyl mono sulphonate</p>	5% at pH 2	Protected and unprotected N-benzyl disulphonate did not adsorb Cd^{2+}	Weltowski et al., 1996
	Fig. 15	High rate of adsorption over Cu^{2+}	Capacities affected by acidity of the medium	Kang et al., 1996
	 <p>Chitosan Mercaptosuccinate</p>	43% metal bound from 50 ppm solution at pH	Less soluble than chitosan at low pH	Lasko et al., 1993
Cd^{2+}	 <p>Thiirane Chitosan</p>	28% from 50 ppm solution at pH 5 on 100 mg derivative	Less soluble than chitosan at low pH	Lasko et al., 1993

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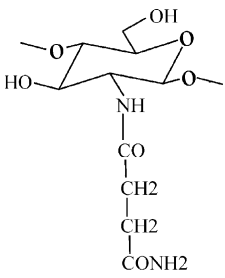
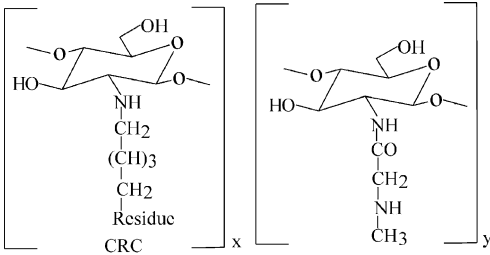
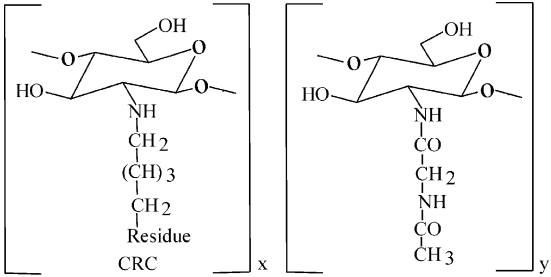
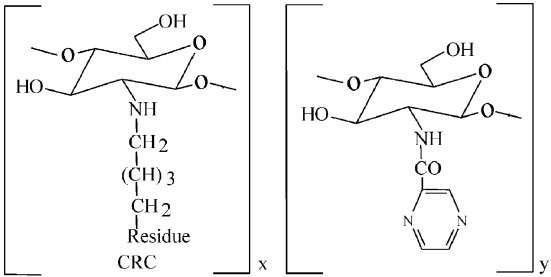
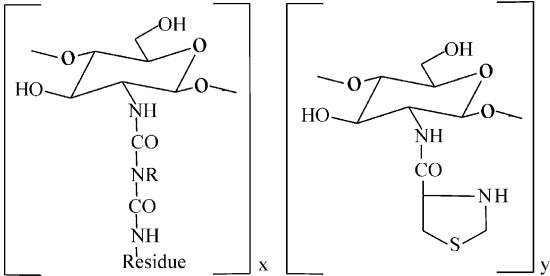
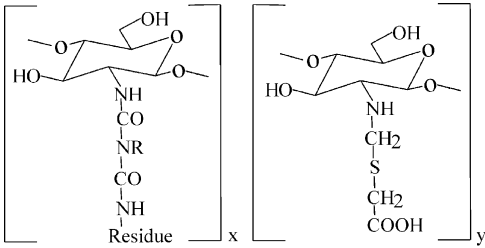
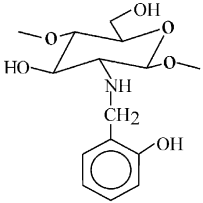
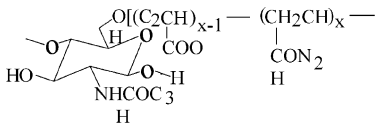
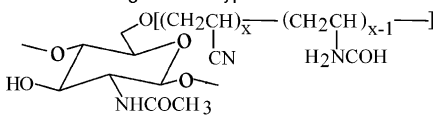
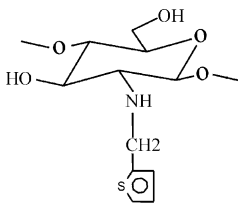
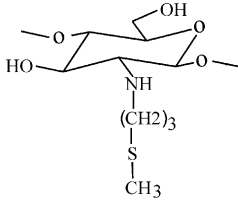
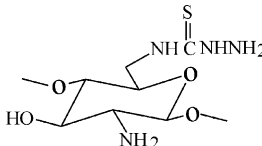
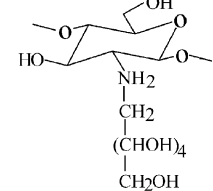
Metal	Structure of The Derivative	Binding Capacity	Remarks	Reference
	<p>Fig. 5</p>  <p>Succinamide-chitosan</p>	<p>27% bound from 50 ppm solution at pH 5 on 100 mg derivative</p>	<p>More solubility than chitosan at low pH</p>	<p>Lasko et al., 1993</p>
	 <p>N-methyl glycine derivative of crosslinked chitosan</p>	<p>1 mmol/g from sulphate, 0.5 from nitrate, 0.2 from chloride solution</p>	<p>Slight improvement in the binding capacities as compared to crosslinked chitosan, metal uptake is higher from sulphate solution than nitrate and chloride solution</p>	<p>Becker et al., 2000</p>
	 <p>N-acetyl glycine derivative of crosslinked chitosan.</p>	<p>0.9 from sulphate, 0.5 from nitrate, 0.2 from chloride solutions</p>		
Cd ²⁺	 <p>Pyrazine-2-carboxylic acid derivative of crosslinked chitosan</p>	<p>0.9 mmol/g from sulphate, 0.4 mmol/g from nitrate, 0.2 mmol/g from chloride solutions</p>		<p>Becker et al., 2000</p>

Table 4 (continued)

Metal	Structure of The Derivative	Binding Capacity	Remarks	Reference
	 <p>R(thiazolidine-4-carboxylic acid) derivative of crosslinked chitosan</p>	1.3 mmol/g from sulphate, 1.1 mmol/g from nitrate, 1.0 mmol/g from chloride		
	 <p>Chitosan product with thioglycolic acid and formaldehyde</p>	0.7 from sulphate, 0.9 from nitrate, 0.7 from chloride		
Zn ²⁺	Fig. 26	0.8 mmol/g from sulphate, 0.1 from nitrate at pH 6		Becker et al., 2000; Weltowski et al., 1996
	Fig. 27	1.4 mmol/g from sulphate, 0.3 mmol/g from nitrate, 0.05 mmol/g from chloride		
	Fig. 28	1.2 mmol/g from sulphate, 0.2 mmol/g from nitrate		
	Fig. 29	1.4 mmol/g from sulphate, 1.1 mmol/g from nitrate, 1.2 mmol/g from chloride		
	Fig. 30	0.9 mmol/g from all three solutions		
	Fig. 22	7% removal from 5 ppm solution		
	Fig. 12	2 mmol/g polymer at pH		Bernkop et al., 1997
Zn ²⁺	 <p>Salicylaldehyde chitosan</p>		Selectivity in presence of Co	
	Fig. 16		Higher adsorption as compared to chitosan and Fig. 31 at pH 7	Ma et al., 2000
Pb ²⁺	Fig. 14	99.5% from 100 ppm solution		Kawamura et al., 1993
	Fig. 23	49% removed from 50 ppm solution at pH 5 on 100 mg derivative	Five times increase in the binding capacity as compared to chitosan	
	Fig. 24	27% removal from 50 ppm solution at pH 5 on 100 mg derivative	Three times increase in the binding capacity as compared to chitosan	
	Fig. 5	21% removed from 50 ppm solution at pH 5 on 100 mg derivative	Two times increase in the binding capacity as compared to chitosan	
	Fig. 22	12% removed from 5 ppm solution at pH 2 on 100 mg derivative		Weltowski et al., 1996
	Fig. 31		Selective in presence of Co	
	Fig. 8	11.1% removed from	Selective in presence of Ni ²⁺	
	Fig. 9	25.4 removed from	Selective in presence of Cu ²⁺ and Ni ²⁺	Tan et al., 1999
Mn ²⁺	Fig. 16	99–100% removal from 100 ppm solution on 110 mg of conjugates	All the eight conjugates showed high adsorption unlike chitosan which showed 7% binding for Mn	

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Table 4 (continued)

Metal	Structure of The Derivative	Binding Capacity	Remarks	Reference
Cr ³⁺	Fig. 22 Fig. 21  Chitin graft PAN Type 2  Chitin graft PAN Type 3	43% removed from 5 ppm solution 1980 pp/g polymer at pH 3.5 2210 ppm/g polymer at pH 3.5		Weltowski et al., 1996 Aly et al., 1997
	Fig. 16 Fig. 4  Thienyl methyl chitosan  Methyl thiopropylchitosan	70% removed from 100 ppm solution on 100 mg polymer at pH 7 5.8 mmol/g polymer 4.8 mmol/g polymer	Selective over Cu, Ni, Zn, Cd, Fe 2.5–3 times as compared to crosslinked Cu complexed chitosan	Kawamura et al., 1993 Baba et al., 1996 Baba et al., 1996
Pd ²⁺	Fig. 10 Fig. 11	0.039 g/g adsorbent 0.033 g/g adsorbent 0.048 g/g chitosan	Selective over Pb and Cr; Adsorption capacity was lower than chitosan Selective over Pb and Cr; Adsorption capacity was lower than chitosan	Peng et al., 1998 Peng et al., 1998
Pt ⁴⁺	Fig. 8		Selective over Cu, Ni, Co, Zn, Cd, Fe	Baba et al., 1996
Hg ²⁺	Figs. 4 and 9 Fig. 14  Chitosan thiosemi-carbazide.	100% removed from 100 ppm solution at pH 7 on 100 mg polymer	Higher selectivity than Fig. 24 Highest selectivity for Hg in presence of UO ²⁺ and Cu ²⁺	Baba et al., 1996 Kawamura et al., 1993 Choi, 1990
UO ²⁺	Fig. 14 Fig. 33 Chitosan phosphate	99.9% from 100 ppm solution at pH 7 on 100 mg polymer UO ²⁺ < Hg ²⁺ 95.8% from 0.0001 M solution on 20 mg derivative		Kawamura et al., 1993 Choi, 1990 Sakasguchi et al., 1981
Ga ³⁺ , In ³⁺	 D-galactose modified chitosan Ga > In > Nb > Eu > Cu > Ni > Co Fig. 12 Ga = In = Fe > Cu > Ni > V > Zn = Co > Al > > Mn			Kondo et al., 1996 The order of selectivity was

The DSC curve of chitosan–metal chelates shows two peaks: an endothermic peak at 100 °C and an exothermic peak at 310 °C (Nieto & Peniche-Covas, 1991). The glass transition temperature of chitosan was observed to be 203 °C. The two peaks in the DSC curve are due to vaporization of water in the polymer and oxidative degradation as well as deacetylation (Qu, Wirsén, & Albertsson, 2000).

Hg²⁺, Cu²⁺ and Fe³⁺ complexes of chitosan had been characterised by DSC (Sreenivasan, 1996). It was observed that there was a small increase above the chitosan in the decomposition temperature of these metal complexes. This was considered to be the effect of two opposing factors: (a) conformational changes of chitosan leading to thermal instability, and (b) additional bridging through metal ion leading to enhanced thermal stability. It was observed that Hg²⁺ complex showed three endothermic transitions at 206, 220 and 242 °C while Cu²⁺ complex showed a single peak at 203 °C, which could be due to formation of a new crystalline phase.

2.8.4. IR and NMR

Infra red (IR) and nuclear magnetic resonance (NMR) techniques are the most commonly used to determine the active sites in chelate formation. A study of chitosan–Schiff's bases, viz. mixed salicylidene and benzylidene derivatives and their complexes with Cu²⁺ showed that in presence of Cu²⁺ the carbon signals due to salicylidene chitosan disappeared and those of benzylidene chitosan were broadened significantly thus showing that benzylidene chitosan did not take part in chelate formation. It was also shown that the presence of paramagnetic ions affects the resolution significantly (Hall & Kim, 1986).

Coordination of fully deacetylated chitosan with Zn²⁺ showed the involvement of amine and secondary hydroxyl group chitosan in chelate formation. Also shifts in the band at 3420 cm⁻¹ due to OH and NH₂ groups to 3391 cm⁻¹, in the 1597 cm⁻¹ band (-NH stretching) to 1620 cm⁻¹, and shift in 1098 cm⁻¹ band (sec OH stretching) to 1062 cm⁻¹ supported the above data. There was no shift in the band at 1038 cm⁻¹ (primary OH), which suggested that primary hydroxyl was not involved in chelate formation. IR spectrum of chitosan–Cu²⁺ complex revealed that the secondary hydroxyl and amine coordinated to Cu²⁺ and new peaks were observed at 555, 532, 551, and 511 cm⁻¹. The peak at 550 cm⁻¹ corresponds to asymmetric Cu–O vibration and 511 cm⁻¹ corresponds to hydroxy-bridged complex (Wang, Zhou, & Yu, 2000).

2.8.5. Circular dichroism

It was observed that chelation of metal ions introduced new bands in the circular dichroism (CD) spectra *N*-carboxymethyl, *N*-carboxybenzyl as well as *N*-alkyl chitosans (Muzzarelli & Tanfani, 1982; Muzzarelli, 1983a,b).

2.8.6. Thermogravimetric analysis

Thermogravimetric analysis (TGA) has been used to study the chitosan–Ag⁺ complex and it was observed that chitosan became thermally less stable after forming the complex (Peniche-Covas, Jimenez, & Nunez, 1988). It was also seen that only 52% of the Ag⁺ present was complexed with chitosan while remaining was retained by sorption.

Chitosan–Cu²⁺ complexes at pH 5, 6 and 7 were studied by TGA. Chitosan showed three steps in thermograms while complexes showed four steps (Wang et al., 2000).

In this review we have presented examples of the various types of chitosan derivatives synthesized so far and the selectivity they exhibit towards various metal ions. The same data can also be presented in a useful tabular form showing each metal ion against the various chitosan derivatives that can complex it, along with the binding capacity of that derivative (Table 4).

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