

3 The Sorbents: Chitin, Chitosan and Derivatives

3.1 Structure of Chitin and Chitosan

Chitin is one of the most abundant organic materials, being second only to cellulose in the amount produced annually by biosynthesis. It occurs in animals, particularly in crustacea, molluscs and insects, where it is a major constituent of the exoskeleton, and in certain fungi, where it is the principal fibrillar polymer in the cell wall. Chitin has a crystalline structure and it constitutes a network of organised fibres, this structure confers rigidity and resistance to organisms that contain it (Roberts 1992).

Chitin is poly[β -(1 \rightarrow 4)-2-acetamido-2-deoxy-D-glucopyranose], and its idealised structure is shown in Figure 3.1.

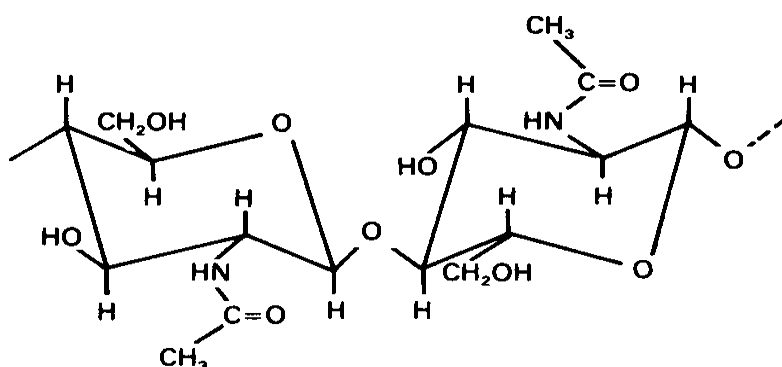


Figure 3.1: The structure of chitin.

The principal derivative of chitin is chitosan, produced by alkaline deacetylation of chitin. Chitosan also occurs naturally in some fungi but its occurrence is much less widespread than that of chitin. Chitosan is poly[β -(1 \rightarrow 4)-2-amino-2-deoxy-D-glucopyranose] and its idealised structure is shown in Figure 3.2. The typical commercial chitosan has approximately 85% deacetylation.

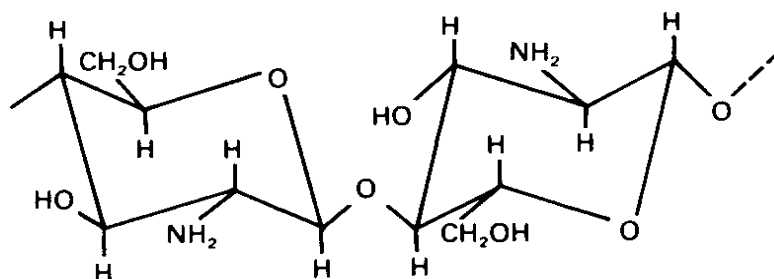


Figure 3.2: The structure of chitosan

Thus the terms chitin and chitosan describe a continuum of copolymers of N-acetyl-D-glucosamine and D-glucosamine residues, the two being distinguished by insolubility or solubility in dilute aqueous acid solutions. Their properties are frequently dependent on the relative proportions of N-acetyl-D-glucosamine and D-glucosamine residues, as are their biodegradability and their biological role.

3.2 Preparation of Chitosan

3.2.1 Purification of Chitin

The main sources of material for laboratory preparation of chitin are the exoskeletons of various crustacea, principally crab and shrimp. In these, chitin is closely associated with proteins, inorganic material which is mainly CaCO_3 pigments and lipids. Various procedures have been adopted to remove these impurities. Demineralisation is most frequently carried out by treatment with HCl and deproteinisation by treatment with NaOH, but other methods may be used and the order in which these two steps are carried out has varied with different workers, although in most instances deproteinisation has been carried out prior to demineralisation. The use of enzymes for protein removal has been examined by a number of workers (Roberts 1992). Broussignac (1968) suggested the use of enzymes such as pepsin or trypsin if the chitin is required to be as fully N-acetylated as possible, but no experimental details were given.

The choice of processing conditions may be governed to some extent by the purpose for which the chitin is required, since partial deacetylation during deproteinisation is not a disadvantage if the chitin is subsequently to be converted to chitosan, while some hydrolysis of the polymer chain during the demineralisation process can be tolerated if chitin is to be used in the form of particles or converted to microcrystalline chitin.

The exoskeletons of crustacea contain colouring matter, principally carotenoids, which do not appear to be complexed with either inorganic material or protein, since treatments which remove these components do not remove the carotenoids. However, they may be removed by extracting the shell with ethanol or acetone after demineralisation. Alternatively, the colouring matter may be destroyed by bleaching and the use of KMnO_4 or H_2O_2 (Broussignac 1968; Roberts 1992).

3.2.2 Deacetylation of Chitin

One of the main reactions carried out on chitin is deacetylation, most commonly by using aqueous alkali. The most frequently used alkali is NaOH. The extent of deacetylation is governed by the alkali concentration, temperature, time of reaction, particle size and density. While treatment with 50 wt- % NaOH at 100°C for 1 hour gave a product having 82% deacetylation, extending the reaction time to 48 hours enabled almost 100% deacetylation to be achieved. However this was at the expense of a considerable decrease in solution viscosity, indicating chain degradation (Roberts 1992).

Other variations on the standard aqueous alkali treatment to avoid chain degradation have been directed towards reducing the quantity of alkali required in the treatment. Batista and Roberts (1990) suggested the use of water-miscible solvents such as 2-propanol or acetone as a diluent to ensure ease of stirring, and as a transfer medium to ensure uniform distribution of the

aqueous alkali throughout the chitin mass. These solvents decrease the depolymerisation of chitosan.

3.3 Physicochemical Characteristics of Chitosan

3.3.1 Degree of N-acetylation

Chitosan is characterised by either the degree of acetylation (DA), which corresponds to the N-acetylamine groups, or the degree of deacetylation DDA (DDA=100-DA), D-glucosamine groups.

The degree of acetylation has an influence on all the physicochemical properties, (molecular weight, viscosity, solubility, etc...) so, it is one of the most important parameters. Many techniques have been tried in order to determine the degree of acetylation more precisely (Roberts 1992). The most appropriate technique for rapid characterisation seems to be the IR spectroscopy.

3.3.2 Molecular Weight

The definition of average molecular weight of polysaccharides and the understanding of its consequences on their physicochemical behaviour have presented a real challenge to chemists for a number of years. In the case of chitin and its derivatives, knowledge of such data is very important for industrial uses and for advanced research in numerous fields. Although the primary structure of chitosan is a backbone of (1→4)-β-D-glucosamine residues randomly acetylated to various extents, the name chitosan is in fact a collective term for deacetylated chitins differing in terms of crystallinity, optical characteristics, degree of acetylation, impurity content, and average molecular weights.

Production methods and origins are mainly responsible for the above differences, which are encountered in various chitosans. If quality-control

standards are sought for properly characterised chitosans, especially for use in specialty applications, a reliable method of molecular-weight determination is desirable. Methods currently used are based on viscometric measurements (Roberts 1992).

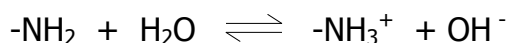
More recently, size exclusion chromatography (SEC), also known as gel permeation chromatography (GPC) or gel filtration chromatography (GFC) has been applied to the study of molecular weight and molecular weight distribution of synthetic polymers, biopolymers and natural polymers. The retention of components is based on the size in solution in which the largest molecules are excluded from the stationary phase pores and elute earlier in the chromatogram. The smaller molecular weight components enter the stationary phase pores and, as a result, elute later in the chromatogram. SEC is utilised to qualitatively determine the molecular weight differences between two lots of the polymers, or quantitatively determine the number, weight, average molecular weights and polydispersity. Both aqueous and organic mobile phases are utilised in separate separations. Available detectors include differential refractive index (IR) and multi-angle light scattering (MALLS). With the IR detector, molecular-weight is determined by standard curves generated with polymers of well-defined molecular weight. With the MALLS detector, molecular weight is determined directly based on light scattering.

In this study chitosan was supplied by ABER-Technologie (France) as a flaked material, with a deacetylation percentage c.a. 87%, defined by FTIR spectrometry (Roberts 1992). The mean molecular weight was measured at 125000, using a size exclusion chromatography (SEC) method coupled with a differential refractometer and a multi-angle laser light scattering photometer (Piron et al. 1997; Milot et al. 1998).

3.3.3 Solubility

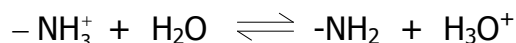
Chitosan in the form of free amine is insoluble in water to pH near neutrality, in concentrated acids with the exception of sulphuric acid, the bases and organic solvents. Their acid base properties allow easy dissolution. Therefore, chitosan is soluble in dilute HCl, HBr, HI, HNO₃, and HClO₄. Chitosan is also slightly soluble in dilute H₃PO₄ but is insoluble in dilute H₂SO₄ at room temperature, although chitosan sulphate dissolves in water on heating and reforms on cooling.

In fact, chitosan is soluble in diluted acids on account of a protonation of free amine groups. The dissociation constant K_b , of an amine group is obtained from the equilibrium



$$k_b = \frac{[-\text{NH}_3^+][\text{OH}^-]}{[-\text{NH}_2]} \quad \text{and } \text{pk}_b = -\log k_b$$

While the dissociation constant of the conjugated acid is obtained from the equilibrium



$$k_a = \frac{[-\text{NH}_2][\text{H}_3\text{O}^+]}{[-\text{NH}_3^+]} \quad \text{and } \text{pk}_a = -\log K_a$$

As in all polyelectrolytes, the dissociation constant of chitosan is not, in fact, constant but depends on the degree of dissociation at which it is determined. The variation of the pk_a value can be calculated using Katchalsky's equation (Roberts 1992)

$$\text{pk}_a = \text{pH} + \log \left(\frac{(1-\alpha)}{\alpha} \right) = \text{pk}_0 - \frac{\varepsilon \Delta \Psi(\alpha)}{k_T}$$

where $\Delta \Psi$ is the difference in electrostatic potential between the surface of the polyion and the reference, α is the degree of dissociation, k_T is Boltzman's

constant and ε is the electron charge. Extrapolation of the pK_a values to $\alpha = 1$, where the polymer becomes uncharged and hence the electrostatic potential becomes zero, enables the value of the intrinsic dissociation constant of the ionisable groups, pK_0 , to be estimated. The value obtained, ~ 6.5 , is independent of the degree of N-acetylation, whereas the pK_a value is highly dependent on this factor. The pK_0 is called the intrinsic pK_a of the chitosan. Therefore, the solubility of chitosan depending on its degree of dissociation and the method of deacetylation used.

3.3.4 Crystallinity

Ogawa and Yui (1993) and Ogawa (1991) stated that the three structural forms of chitosan (hydrated and anhydrous crystal, and non-crystal) could be examined easily by measuring the X-ray powder diffraction pattern of a chitosan sample. The hydrated crystal showed a strong reflection at an angle (2θ) of 10.4° degrees and the other peaks more weakly at 20° and 22° . The anhydrous crystal exhibited a strong peak at 2θ of 15 degrees and a peak supplementer at 20° . An amorphous chitosan does not show any reflective, but they ascertained that it exhibits a broad halo at 2θ of around 20° .

Piron et al. (1997) reported that the dissolution of chitosan involves the progressive disappearance of the peak at $2\theta \approx 22^\circ$ and suggested that polymer swelling destroys the residual crystallinity, increasing the accessibility of solute to sorption sites. They showed that uranyl sorption by chitosan flakes is affected by polymer hydration kinetics and by the crystallinity of the material. Ogawa (1991) attributed the loss of native crystallinity to the chitosan dissolving.

Kurita et al. (1988), substituting nonaoyl groups on chitosan, observe that the crystallinity decreases at a low substitution level while it increases again at high substitution levels. They attribute the variation in copper sorption capacities to this grafting and to the variation in crystallinity.

Ogawa and Yui (1993), comparing partially N-deacetylated chitin and partially N-acetylated chitosan, observed that these modified forms of chitosan are less crystalline than pure deacetylated chitosan, and that N-acetylation of pure chitosan involves the production of less crystalline samples than solid-state deacetylation of chitin.

Guibal, Milot and Roussy (1999) showed that the maximum sorption capacity for the molybdate depends mainly on the crystallinity and degree of deacetylation of chitosan; the worst sorbents are characterized by higher crystallinity index (appearance of a band on the X-ray diffraction at around $2\theta = 22^\circ$). In order to decrease sorbent crystallinity they proposed that chitosan gel beads be used instead of flaked particles.

3.4 Derivatives of Chitosan and Complexant Properties

3.4.1 Introduction

Chitosan is a polysaccharide which, thanks to its reactive properties, can produce numerous derivatives having a wide range of uses.

Chitosan can carry a large number of amine groups on its chain, and thus form multiple complexes. At acid pH, the protonated form, it can associate with polyanions to form complexes. At higher pH levels (over 4) it can form complexes with colorants and heavy metals. The presence of the pair of free electrons of the amine group is assumed to be the origin of the dative bonds, an idea confirmed by the observation of a much weaker fixation in chitin. However, there may be interaction due to the simple phenomenon of adsorption, electrostatic attraction or ion exchange. The environment of the amine function affects its effectiveness in terms of complexation.

Chitosan is therefore a well-known biosorbent of metal ions. Several studies have been carried out on its sorption capacity, using native chitin or chitosan (Muzzarelli and Tubertini, 1969; Muzzarelli, 1973, 1977) or more sophisticated forms resulting from a grafting of specific functional groups (Muzzarelli et al. 1984; Guibal et al. 1995).

Preliminary work on metal ion biosorption have been performed mainly on fungal or bacterial biomass. These studies have shown that metal ions are retained, mainly in the cell wall. As the functional groups that are most abundant in the cell wall are mainly amine functions, hydroxyl groups, phosphate groups or carboxylic groups, it not surprising that the search for new derivatives of chitosan that improve on its adsorption capacity has developed along the lines of incorporating carboxylic groups, and phosphates groups and increasing the amount of amines in the chitosan, as these are the groups that interact with metal ions.

It is also well known that chitosan can dissolve in either organic or mineral acids. This is a restrictive parameter for industrial applications in waste water treatment. A crosslinking procedure can be used to reinforce the chemical and mechanical properties of chitosan using different chemical reagents.

Some of the most representative derivatives are set out below, paying special attention to those that have been used for the recovery and separation of metals from the platinum group.

3.4.2 Crosslinked Chitosan

In order to avoid dissolution in aqueous acid solution, crosslinking between polymer chains has been proposed; however, it is expected that the crosslinking produces a significant decrease in the adsorption capacity, due to the formation of chemical bonds at the adsorption sites. Ohga et al. (1987) successfully overcome this idea by crosslinking chitosan after complexation with

metal ions to prepare chitosan-based adsorption gels that are insoluble in aqueous solutions without losing their high adsorption capacity. This concept is similar to that proposed by Nishide et al. (1976), who prepared crosslinked poly(4-vinylpyridine) resins with high selectivity to the metal ion that was used as the template. It is therefore expected that the crosslinking metal-complex chitosan will show not only a high loading capacity that is nearly equal to that of the original chitosan, but also high selectivity of the metal ion employed as the template.

Inoue et al. (1993) have compared the different adsorption between original chitosan, crosslinked copper(II)-complexed chitosan and chitosan crosslinked by hexamethylenediisocyanate. The copper(II)-complexed chitosan is crosslinked with epichlorohydrin using a partly modified method to that proposed by Ohga et al. (1987). In this work on the ammonium nitrate solution, the results demonstrate that the amount of copper(II) ions adsorbed on the original chitosan is greater than that on crosslinked copper(II)-complexed chitosan. For hydrochloric acid solutions, in the case of platinum(IV), the variation in adsorption capacity for the crosslinked copper(II)-complexed chitosan is only slightly less than that for the original chitosan, while for palladium(II) there appears to be no significant difference between the two adsorbents. However, the adsorption on the chitosan crosslinked with hexamethylenediisocyanate is considerably less than that of the other two adsorbents, not only for palladium, but also for platinum.

Fuji Spinning Co., Ltd. (1989), also propose the utilization of diisocyanate compound as a reticulant agent for improving the chemical resistance to acid and alkali media.

Crosslinking with glutaraldehyde occasionally produces different results. Yang and Zall (1984) and Masri et al. (1978) indicated that heterogeneous crosslinking of chitosan powder with glutaraldehyde did decrease adsorption capacity but prevented chitosan solubilization. On the other hand, Koyama and

Taniguchi (1986) performed homogeneous crosslinking of chitosan with glutaraldehyde in acetic acid solutions, precipitated the product and then found that crosslinking actually increased adsorption capacity for Cu(II), with a reagent CHO/NH₂ ratio of 1 being optimum.

Glutaraldehyde crosslinking occurs through a Schiff's base reaction between aldehyde ends of the crosslinking agent and amine moieties of chitosan to form imine functions (Roberts, 1992; Rorrer et al. 1993; Guibal et al. 1998) as shown in the Figure 3.3.

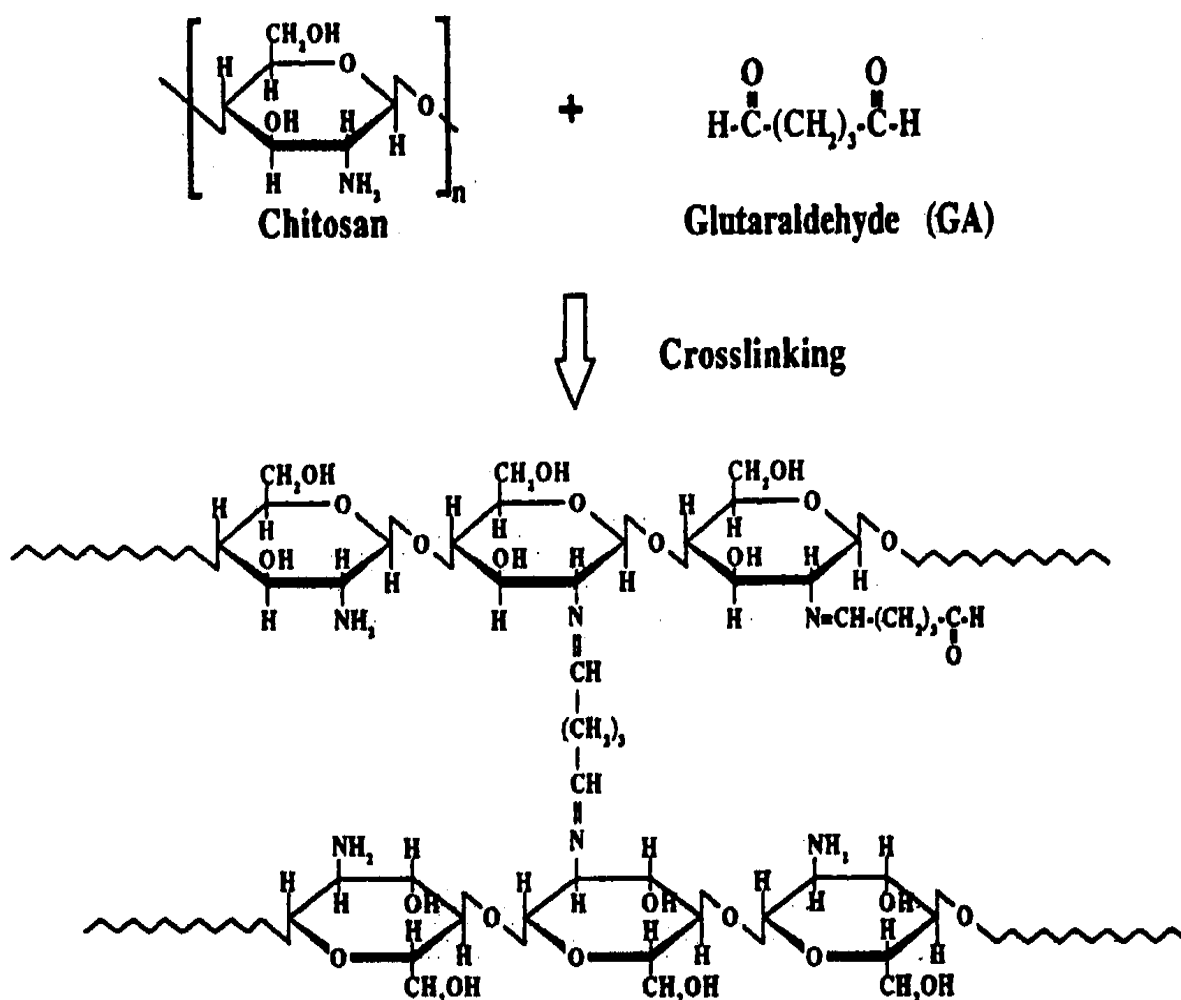


Figure 3.3: The structure of crosslinked chitosan.

Glutaraldehyde has been used by several groups for cadmium recovery on chitosan beads (Rorrer et al. 1993), molybdenum and vanadium sorption (Guibal et al. 1998). This adsorbent has been widely experimented with for noble metal groups, both in its original form, and after chemical modification (Tong et al. 1991; Baba and Hirakawa, 1992; Inoue et al. 1995; Ni and Xu, 1996; Wan Ngah and Liang, 1999; Guibal et al. 1999a).

Other reticulant agents include ethylene glycol diglycid ether (Fuji Spinning Co., Ltd. 1989) and dicarboxylic acid or acid anhydride, such as itaconic anhydride, or maleic anhydride or citraconic anhydride (Virginia Tech Intellectual Properties, Inc., 1999).

3.4.3 Carboxylate Derivatives

The insertion of carboxylic functions in chitosan has been widely studied. The preparation of carboxymethylchitosan by reacting chitosan and chloroacetic acid in an alkaline medium was one of the first techniques to be used. The preparation of *o*-carboxymethylchitosan involves swelling the chitin in dimethylsulfoxide, treatment with a concentrated sodium hydroxide solution, reaction with monochloroacetic acid, and deacetylation in hot sodium hydroxide. Numerous studies have been conducted to obtain carboxyalkylchitosans. These include those carried out by Muzzarelli and coworkers over a period of years. In these derivatives, the principle of transformations refers to a reaction of by means of Schiff's reaction. The reaction between the carboxylic group present in organic acid and the chitosan amine group leads to the formation of a ceto-imine with low stability. This intermediary was then reduced with sodium cyanoborohydrine or sodium borohydrure, in order to obtain a substitute chitosan which was stable and insoluble, under the conditions of use in the treatment of low concentration industrial effluent. They have proposed substituting the different acids such as oxalacetic acid, glyoxylic, β -hydroxypyruvic acid (Muzzarelli and Rochetti, 1986) or phthalaldehydic acid (Muzzarelli and Tanfani, 1982) on the chitosan, in order

to obtain aspartate glucan, glycine glucan, serine glucan and N-carboxybenzylchitosan, respectively. These bioadsorbents are characterised by their high efficiency in fixating cobalt and copper.

Saucedo et al. (1993) have proposed the synthesis of modified polymers such as N- [2-(1,2-dihydroxyethyl)tetra-hydrofuryl] chitosan, N. D. T. C. and glutamate glucan for application to uranium sorption. The modified polymers were synthesized in accordance with a procedure quite similar to that proposed by Muzzarelli (1985), which consists, as mentioned above, of a two-step mechanism: first, solubilization of chitosan in organic acid which promotes the ketoimination of the polymer, and a second step which leads to the reduction of this intermediary product.

More recently Inoue et al. (1995) proposed obtaining the monocarboxymethylated chitosan with monochloroacetic in ethanol; in this work, these authors also present synthesis of N, N-dicarboxymethylated chitosan and the diethylenetriaminopentaacetic acid type of chitosan. These sorbents have been utilized to examine the adsorption of palladium (II), platinum (IV), iridium (III) and rhodium (III) from a hydrochloric acid solution.

3.4.4 Sulphur Derivatives

The grafting of donor S groups is less well documented. Ni and Xu (1996) have proposed the synthesis of a series of crosslinked chelating resins based on chitosan, containing amino and mercapto groups. In this study, chitosan was first reacted with chloromethyl thirane (CT) to synthesize PCS resins. After the reaction of this product with N,N-Diethylaminomethyl thirane (SN) the resin PCSSN was obtained and by substituting epichlorohydrin and N,N-Diethylaminomethyl oxirane (ON) for CT and SN, they synthesized the resin PCONN. With these resins they investigated the adsorption capacities, adsorption rates, and adsorption selectivities for Ag(I), Au(III), Pd(II), Pt(IV), Cu(II), Hg(II) and Zn(II). The results indicate that these resins have

remarkable adsorbing capacities and adsorption rates for four noble metal ions and Hg(II).

Argüelles-Monal and Peniche-Covas (1993) investigated the grafting of mercapto groups on chitosan for mercury removal. More recently, Binman et al. (1997) studied the fabrication of sulphur-chlorinated compounds derived from jojoba wax bound to polystyrene beads for mercury and chromate recovery. They showed that the grafting on these sulphur derivatives is characterized by an enhanced selectivity and efficiency for metal recovery from brines and complexes solutions.

Guibal et al. (2002) have demonstrated that sorption performances are enhanced by the modification of chitosan through the grafting of sulphur compounds (thiourea, rubeanic acid) on chitosan backbone using glutaraldehyde as a linker. This modification allows the sorption capacity to be slightly increased in hydrochloric acid solutions, but the main interest of these new derivatives is related to the lower competition effect of sulphate and chlorine in comparison with glutaraldehyde crosslinked chitosan. The chemical modification involves the ion exchange resin being converted into chelating resin.

The influence of the amount of glutaraldehyde and thiourea on the impregnation bath has been investigated and optimised with special attention to the composition of the solution and the type of acid used for pH control (Guibal et al. 2000).

3.4.5 Phosphorous Derivatives

The insertion of phosphate functions into chitosan has made it possible to develop a wide variety of polymers, soluble and insoluble, which complex and fix metals such as nickel, zinc or cadmium. Thus, the method used by Nishi et al. (1987) consists of making chitosan react with phosphorus pentoxide in

methanesulphonic acid. This procedure triggers the insertion of phosphate groups and sulphonic acid in the chitosan. A cross-linking reaction with adipoylchloride causes precipitation of a solid formed by the links between chains. The polymer obtained is characterized by a high phosphorus content, ranging from 7 to 12%. The degree of substitution depends essentially on the degree of deacetylation of the chitosan. This product is substantially more stable than the chitosan in acid media, but presents a significant decrease in fixation efficacy.

A novel water-soluble chitosan derivative carrying phosphonic groups was synthesized by Heras et al. (2001). In this work the authors introduced the new derivative and told about its properties over the sorption of metals but not details for the sorption of precious metals were given.

3.4.6 Acylation

The simplest example of N-acylation of chitosan is, of course, the production of completely N-acetylated chitin.

N-acylation of chitosan can randomly add hydrocarbon side chains to a fraction of the amine groups. These hydrocarbon side chains can impart a hydrophobic substructure to the biopolymer and also disrupt the hydrogen bonding network between chitosan chains to expose more amine sites for binding with metal ions. Kurita et al. (1988) have proposed the introduction of nonanoyl groups, $\text{CH}_3(\text{CH}_2)_7\text{CO}-$, and also the influence on adsorption behaviour in comparisons with those of acetyl groups in adsorption of copper (II) ions.

In a more recent study, Hsien and Rorrer (1995) has presented the effect of modifying chitosan via N-acylation and the effect of crosslinking with glutaraldehyde. As with N-acylation, crosslinking also can increase the spacing between of the chitosan chain to improve the accessibility of metal ions to

amine sites. Both acylation with nonanoyl chloride, $\text{CH}_3(\text{CH}_2)_7\text{COCl}$ and crosslinking with glutaraldehyde attempted to impart hydrophobicity to the biopolymer and to increase the spacing in the biopolymer chain, in order to reduce solubility and improve access of transition metal ions to amine adsorption sites. In this work the combination of acylation, bead casting, crosslinking and freeze-drying steps produced highly porous chitosan beads.

3.4.7 Incorporation of Complementary Amine Functions

Another technique to improve the sorption efficiency of chitosan after a cross-linking treatment consists of the incorporation of complementary amine functions. This procedure has been used by Baba and Hirakawa (1992) and Kawamura et al. (1993). Baba and Hirakawa showed in this work the sorption characteristics of N-(2-pyridylmethyl)chitosan, which is synthesized by crosslinking the n-(2-pyridylmethylidene)chitosan with (chloromethyl)oxirane, and they proposed its application to the commercial separation and purification of palladium(II), platinum(IV) and mercury(II) from hydrochloric acid containing base metals. Kawamura et al. proposed the grafting of PEI, poly(ethylene imine), on chitosan beads. They crosslinked chitosan beads with ethylene diglycidyl ether (another bifunctional reagent) and then reacted the derivative with epichlorhydrine, and finally the product was reacted with PEI. The adsorption capacity was increased by polyamination with poly(ethylene imine) (MW=10 000). The capacity was about 1-2 times larger than that of commercial chelate resins. The selectivity for adsorption of metal ions on the resin, which was determined for a single solute at $\text{pH} \approx 7$, was $\text{Hg(II)} > \text{UO}_2(\text{II}) > \text{Cd(II)} > \text{Zn(II)} > \text{Cu(II)} > \text{Ni(II)}$. Mg(II) , Ca(II) , Ga(III) , As(III) , and Sr(II) were not adsorbed on the resin at all.

Juang and Ju (1997, 1998) have used these polyaminated chitosan beads to examine their sorption behaviour for Cu-EDTA chelate anions from dilute solutions.

3.4.8 Other Derivatives

The synthesis of the two new crosslinked-crown ethers (CCTS-N=CH-B-15-C-5) and (CCTS-N=CH-B-18-C-6) by the reaction of crosslinked chitosan (CCTS-NH₂) with 4'-formyl benzo-15-crown-5 and 4'-formyl benzo-18-crown-6 was presented by Peng et al. (1998). They studied the adsorption and selectivity properties of these crosslinked chitosan-crown ethers for Ag(I), Pd(II), Pb(II), Cd(II) and Cr(III). The experimental results showed that the two crosslinked chitosan-crown ethers not only have good adsorption capacities for Ag(I) and Pd(II), but also high selectivity for the adsorption of Ag(I) or Pd(II) with the coexistence of Pb(II) and Cr(III).

Alam et al. (1998) have prepared oxine type chemically modified chitosan by the template crosslinking method using modified chitosan by the template method using Fe(III) as a template ion. Batch adsorption of rhodium(III) on this chemically modified chitosan was examined using chloride media in the absence and presence of a large amount of tin(II).

3.5 Different Treatments of Chitosan

3.5.1 Gel

Chitosan-based gels may be broadly divided into thermally non-reversible gels and the far smaller group of thermally reversible gels. Within the first group a further subdivision into those formed by N-acylation and those produced by Schiff's base (aldimide) formation is useful, and this division of the topic is used here.

N-Acylchitosan are prepared treating chitosan in solution acetic acid 10%, or in 5% water-methanol acetic acid and a range of acyl anhydrides including dodecanoic anhydride and also benzoic anhydride, (Moore and Roberts 1980).

The effects of variation in the acetic anhydride: -NH_2 group mole ratio has been investigated by Hirano and Yamaguchi (1976). This study showed that the presence of anhydrous acids increases the rate of N-acylation in the polymer, reducing solubility and allowing gelation to occur. The rate of gelation was found to increase with a corresponding increase in the chitosan concentration, acyl anhydride concentration and temperature, and when the molecular weight of the acyl anhydride decreased.

The most widely studied gel system involving Schiff's base formation is that using glutaraldehyde, which involves covalent cross-linking formation between the chains. Using viscosity measurements to determine the rate of gelation, Roberts and Taylor (1989) found it to be proportional to the chitosan and the glutaraldehyde concentrations and to the temperature, while it is inversely proportional to the acetic acid concentration.

Hirano et al. (1990) reported chitosan-based thermally reversible gels. They prepared these gels by mixing a chitosan solution with a concentration below 2% with a 3% oxalic acid solution. The gels formed melted on heating and gelled on cooling. The melting points were reasonably high, being 88°C and 92°C, and increased when the chitosan concentration was increased. These authors proposed that the mechanism of the formation of the junction points is one of salt formation, similar to that for formation of alginate gels in presence of Ca^{2+} . In a study of partial N-succinylation of chitosan, the same authors noted that the product which contained 35% of the amine acylated groups produced a thermoreversible gel, though no details this were provided.

3.5.2 Solution

By completely mixing chitosan with acetic or formic acids, a viscous biopolymer solution can be obtained. This type of solution displays a particular type of rheological behaviour: the viscosity increases when the chitosan solution is increased and the temperature is reduced (Roberts 1992). It is therefore

possible to produce 1 to 4% solutions in large quantities, while 20% solutions may be produced in large quantities by using chitosans with a low molecular weight. Once the chitosan solution has been obtained, a simple final preparation or coagulation reaction will allow the resulting chitosan to be treated in various ways – for example, for the formation of chitosan membranes and beads.

3.5.3 Membrane

Owing to its solubility in formic or acetic acid, chitosan is suitable for the preparation of membrane. There is interest in making chelating membranes available for preconcentration of trace elements, for selective isolation of certain elements from saline solutions, or for special sample preparations in nuclear chemistry or in electrochemistry. A chelating membrane is expected to exhibit superior characteristics as it would be selective, would not release ions to solution, and would bind transition metals by dative bonds instead of ionic bonds.

The chitosan membranes were described and characterized for the first time by Muzzarelli and co-workers (1974). Chitosan membranes were produced from a solution of chitosan in formic acid. This solution was poured on a glass plate and kept perfectly horizontal upon a water bath. When formic acid was completely evaporated, the glass plate was exposed to cold air so that the membrane could easily be removed from the glass surface. These water soluble chitosan formate membranes were dipped into 1M NaOH. The membrane was then washed with distilled water to neutrality and then placed on a clean glass plate and kept at 60°C until dry.

In addition to a simple technique based on the evaporation of formic acid from chitosan solution spread on a glass plate, these authors proposed another approach for preparing chitosan membranes. A chitinous membrane was reported to occur in the shell of the cuttlefish "Sepia Officinalis". To produce a

chitosan membranes from the "Sepia Officinalis" shell, the isolation procedure included a 10% hydrochloric acid treatment for three or four days, and an ether extraction and deacetylation with KOH in an ethanol+monoethyleneglycol mixture. Both procedures, which involved chitosan powder from crab shells, or the "Sepia Officinalis" membrane, yielded perfectly transparent membranes with a high mechanical resistance.

Chitosan membranes generally show lower capacity than chitosan powder, due to the reduced contact surface; however, collection is good, especially for molybdenum, chromate and mercury.

The chitosan membranes are resistant to both alkaline solutions and many organic solvents (Muzzarelli 1977). Uragami et al. (1994) have analyzed the structure of chitosan membranes which were chemically modified with aldehydes, such as glutaraldehyde and n-butyl aldehyde and their characteristics in terms of permeation and the separation of aqueous ethanol solutions.

Kaminski and Modrzejewska (1997) present an application of chitosan membranes for the removal of heavy metals ions. In this study, the metal ions Cu(II), Cd(II), Co(II), Zn(II), and Ni(II) are almost entirely separated by the membranes. In the case of Cr(VI) and Mn(II) ions, the separation depends on pH and process conditions.

3.5.4 Beads

For the fabrication of beads of gel, the concentration of the chitosan solution can be freely selected according to the molecular weight of chitosan from a point at which it flows easily and can be handled without difficulty. The preferred concentration for the solution is in the range of 2% to 20%. A viscosity regulator such as urea may also be added to the acidic aqueous solution (Fuji, Spinning Co., Ltd, 1989).

The aqueous acidic solution of chitosan is prepared and a predetermined quantity is poured into a coagulating bath through a discharge hole. The pore diameter of the discharge port, pressure, etc. can of course be selected optionally according to the desired particle size. For the coagulating bath, a basic solution may be used. Basic usable material can include alkali material such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, ammonia and ethylene diamine. The basic solution used is prepared by adding the above-mentioned basic material to water or alcohol with a polarity such as methanol and ethanol, or a mixture of water and alcohol. Since the alcohol reduces the surface tension of coagulating bath, it can moderate the shocks during pouring and therefore control the specific surface area. The concentration of the basic solution can optionally be selected according to the concentration of the aqueous acidic solution of chitosan used, or the characteristics of the desired granular porous chitosan.

Rorrer et al. (1993) proposed that, in order to produce the smaller 1-mm beads, the acetic acid/chitosan solution must contain 1 wt % of the surfactant Triton X-100 in order to reduce the surface tension of the droplet formed at the extrusion nozzle tip. In addition, nitrogen was blown through the annular space surrounding the nozzle in order to help shake off the droplet. These two modifications promoted the release of the chitosan droplet from the extrusion nozzle tip and helped to reduce the bead diameter and increase the bead formation rate. Unfortunately, rapid bead formation rates produced tailed or nonspherical beads. This problem was solved by reducing the precipitation bath NaOH concentration from 2 to 0.5 M.

For metal ion sorption applications, the high internal surface area of the porous beads can improve the metal binding capacity and also increase the transport rate of metal ion into the particle. But when chitosan is used as a separator in a industrial scale column, flake and gel chitosan may cause a pressure drop, and they do not offer a high efficiency. In order to reduce this problem, several

authors have proposed reticulation. Several reticulant agents can be used, as it has been shown in section 3.4.2.

Rorrer et al. (1993) demonstrated that chemical crosslinking of the linear chitosan chains with the bifunctional reagent glutaraldehyde can render chitosan insoluble in acidic media and improve resistance to chemical and biological degradation. Crosslinking could also improve the mechanical strength and abrasion resistance of the bead so that the adsorbent is suitable for use in a packed column.

3.6 Review of Sorption of PGM on Chitosan

The Table 4 shows a review of sorption of precious metals on chitosan and chitosan derivatives before this work was started.

Complexane types of chemically modified chitosan (see page 65):

- MCM - chitosan: monocarboxymethylated chitosan.
- IDA - chitosan: dicarboximethylated chitosan.
- DTPA - chitosan: diethylenetriaminopentaacetic acid type chitosan.

Resins containing mercapto and amine groups (see page 65):

- CT: chloromethyl thiirane.
- SN: N,N-Diethylaminomethyl thiirane.
- ON: N,N-Diethylaminomethyloxirane.
- PCS: chitosan + CT.
- PCSSN: chitosan + CT + SN.
- PCOON: chitosan + epichlorhydrin + ON.

Table 4: Bibliographic study for adsorption of precious metals on chitosan.

Sorbent	condition	pH	metal	reticulant agent	sorption capacity mg/g	Refer.
N-(2-pyridylmethyl) chitosan	powder	2(HCl)	Pd(II)	epichlorhydrin	617.1	Baba and Hirakawa 1992
Crosslinked chitosan	powder	2(HCl)	Pd(II)	epichlorhydrin	212.8	
Chitosan crosslinked copper (II)-complexed chitosan	bead	2(HCl)	Pd(II)	hexamethylenediisocyanate	223.4	Inoue et al. 1993
			Pt(IV)	hexamethylenediisocyanate	214.6	
MCM - chitosan	flakes	2(HCl)	Pd(II)	—	319.2	Inoue et al. 1995
			Pt(IV)	—	312.1	
IDA - chitosan	flakes	2(HCl)	Pd(II)	—	393.7	
			Pt(IV)	—	214.6	
DTPA - chitosan	flakes	2(HCl)	Pd(II)	—	234.1	
			Pt(IV)	—	409.7	
DTPA - chitosan	flakes	0(HCl)	Pd(II)	—	22.3	
			Pt(IV)	—	12.68	
			Ir(III)	—	7.7	
			Rh(III)	—	≈ 0	
PCS	powder	2(HCl)	Pd(II)	chloromethyl thiirane (CT)	373.5	Ni and Xu 1996
			Pt(IV)	chloromethyl thiirane (CT)	364.8	
PCSSN	powder	2(HCl)	Pd(II)	CT + SN	413.9	
			Pt(IV)	CT + SN	511.1	
PCOON	powder	2(HCl)	Pd(II)	epichlorhydrin + ON	43.6	
			Pt(IV)	epichlorhydrin + ON	193.1	
Chitosan	powder	2(HCl)	Pd(II)	—	102.1	
			Pt(IV)	—	95.6	
Fe(III)-Templated oxine Type of chemically modified chitosan	powder	0(HCl)	Rh(III) [Sn]/[Rh]=6	glycerolpolyglycidylether	94.7	Alam et al. 1998
Chitosan	powder	0(HCl)	Rh(III)	—	≈ 0	
Chitosan	flakes	2(HCl)	Pd(II)	epichlorhydrin	48.8	Peng et al. 1998
Chitosan-Crown Ethers	flakes	2(HCl)	Pd(II)	epichlorhydrin	38.7	
		4(HCl)	Pd(II)	epichlorhydrin	38.7	
Chitosan	flakes	2(HCl)	Pt(IV)	glutaraldehyde	266.6	Guibal et al. 1999

Chitosan	flakes	2(HCl)	Pt(IV)	glutaraldehyde	304.1	Guibal et al. 2000
		2(H ₂ SO ₄)	Pt(IV)	glutaraldehyde	288.1	
Chitosan	flakes	2(HCl)	Pt(IV)	glutaraldehyde+thiourea	346.2	
		2(H ₂ SO ₄)	Pt(IV)	glutaraldehyde+thiourea	386.9	

The Table 5 shows the study of desorption realized with the sorbents mentioned before.

Table 5: bibliographic study for desorption of precious metals on chitosan.

Sorbent	condition	eluent	metal	% recuperation	Reference
Chitosan crosslinked copper (II)-complexed chitosan	flakes	HCl (conc.)	Pd(II) Pt(IV)	70 5	Inoue et al. 1995
MCM - chitosan	flakes	HCl (conc.)	Pd(II) Pt(IV)	100 45	
IDA - chitosan	flakes	HCl (conc.)	Pd(II) Pt(IV)	95 70	
DTPA - chitosan	flakes	HCl (conc.)	Pd(II) Pt(IV)	80 45	
Fe(III)-Templated oxine Type of chemically modified chitosan	powder	0.5 M HCl + 8 M HNO ₃	Rh(III)	72.5	Alam et al. 1998