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Sulfur-Containing Chitin and Chitosan Derivatives as Trace Metal Adsorbents: A Review

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Chitosan has low uptake for most heavy metals as well as high solubility in monoprotic acids. To address these problems, sulfur-containing functional groups have been introduced to enhance the sorption of heavy metals via formation of strong coordination bonds with heavy metals and also to improve its stability. The approaches to sulfur enrichment to the chitosan structure include grafting of sulfur-containing molecules to C₂ amine or C₆ hydroxyl groups. Crosslinking and grafting agents such as glutaraldehyde and epichlorohydrin have also been used in chitosan modification. In this review, special emphasis is placed on the synthesis pathways of sulfur-functionalization of chitin and chitosan and their metal uptakes. Generally, the uptake of soft acid metals such as Hg(II) and Cd(II) has been shown to increase with increasing sulfur content of modified chitosan. However, other factors such as the availability of thiol and amine groups as well as surface area of the modified chitosan also influence metal sorption.

KEYWORDS: chitosan, chitin, sulfur, heavy metal, wastewater remediation, crosslinking

INTRODUCTION

Contamination of soil and water by metals is of great concern due to the potential detrimental effects on human health and the environment. Trace essential metals such as copper and zinc are needed for normal physiological functioning but they are toxic to organisms if concentrations are too high. Besides these essential elements, known toxic trace metals, such as cadmium, lead, and mercury have been found in polluted wastewater (Kim, 2009). The usual way of treating wastewater is by physical and chemical removal of dissolved and suspended matter. Chemical treatment of metals by using activated carbon adsorption is effective but expensive (Demirbas, 2008). Chemical precipitation is the most cost effective treatment for reducing toxic trace metals to safe levels. This method, however, is not effective in removing trace metals at low concentrations (Juang and Shao, 2002). In addition, this process generates huge amounts of solid wastes containing high levels of metal contaminants that are difficult to valorize and require appropriate storage facilities. Membrane filtration technologies are able to separate solute pollutants effectively but they are very expensive (Wang and Chen, 2009).

Employing natural wastes from agricultural and food processing industries as sorbing agents for contaminants presents an economical alternative for water treatment technology (Gupta et al., 2009). This approach not only saves costs in waste disposal, but may turn waste material into a revenue-generating by-product. However, the feasibility of natural waste as a metal sorbent is limited by its low metal adsorption capacity and the fact that it is difficult to regenerate spent sorbent. These weaknesses in natural waste can be alleviated by structural and chemical modification.

Natural wastes containing cellulosic or chitinous materials have been modified and studied for their use in treating metal polluted wastewater (Barriada et al., 2007; Figueiredo et al., 2005; O'Connell et al., 2008; Wan Ngah and Hanafiah, 2008). This has been especially the case for chitinous waste which has one amide group in every sugar unit. The amide group of chitin also contributes to greater metal uptake in comparison to cellulosic waste materials. The first modification on chitinous material was conducted by Rouget where the elimination of the acetyl group from amide formed the amine group, producing a new material called chitosan (Baldrick, 2010). The amine group of chitosan enables greater metal uptake than the amide group of chitin due to the formation of stronger chemical bonds with metal ions. Furthermore, chemically reactive amine groups are also viable for further modification. Numerous modifications have been made to the amine groups as well as hydroxyl groups of chitosan to obtain desirable properties that are suitable for wastewater remediation. These modifications include introducing crosslinks to enhance the stability of chitosan as well as grafting sulfur-containing molecules onto chitosan to improve chitosan derivatives' metal

uptake selectivity (Ruiz et al., 2002). For example, introduction of sulfur-containing functional groups to chitosan structures (i.e., thiol, thione, and thiolate) enhanced the sorption of soft acid metals such as Au(III), Pd(II), and Pt(IV) and increased stability in acidic condition (Bratskaya et al., 2011).

A number of review articles have been published on the development and potential of chitin and chitosan (Pillai et al., 2009; Roberts, 2008), fundamentals of chitin and chitosan modification (Kurita, 2006; Mourya and Inamdar, 2008) as well as biomedical application of chemically modified chitin and chitosan (Jayakumar et al., 2005; Sashiwa and Aiba, 2004). Reviews on pristine and modified chitosan derivatives and their metal adsorption capacity have been published (Wu et al., 2010). The effects of modification to chitosan were also studied for their adsorption capacities, kinetics, and selectivity of toxic or precious metals (Guibal, 2004). However, no comprehensive review to date has been carried out on the fundamentals of sulfur modification of chitosan in relation to metal adsorption capacity. The application of chitosan as a heavy metal sorbent for wastewater remediation depends on the stability of sorbed metal. Most toxic and precious metals, such as Hg(II), Cd(II), Pb(II), and Pt(IV) ions, are “soft acids.” The introduction of “soft bases” such as sulfur-containing groups to chitosan increases the stability of complexed ‘soft acids’, thus enhancing sorption capacity as well as selectivity. This review will focus on the fundamental approaches to sulfur enrichment of chitosan, introduction of crosslinks to the polymeric structure of chitin or chitosan and their effects on metal adsorption capacities compared to pristine chitosan.

CHITIN

Chitin is one of the most abundant polysaccharides with over 10 gigatons produced annually from exoskeletons of insects and crustaceans alone. Other sources of chitin are the cell walls of fungi (e.g., mushrooms) and endoskeletons of cephalopods such as pens of calamar and squid (Harish Prashanth and Tharanathan, 2007). Chitin is a polysaccharide with a repeating unit of *N*-acetylglucosamine (Figure 1). Chitosan is obtained by alkaline deacetylation (under heating) of chitin using sodium hydroxide or potassium hydroxide (Tolaimate et al., 2003). This material is used as pharmaceutical products as

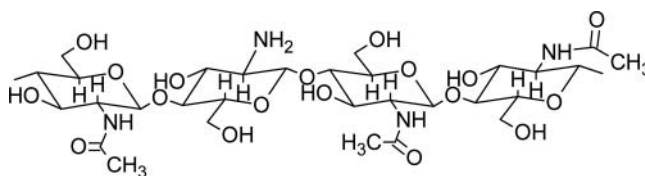


FIGURE 1. Structure of chitin.

well as a potential non-toxic alternative for pest and fungi control (Rinaudo, 2006).

Seafood processing industries provide a huge source of raw materials for the extraction of chitin. Seafood waste is rarely an environmental issue since it can be reused without much processing. Traditionally composted or ground seafood waste has been used as a fertilizer or as a raw material for chitosan production (MacLeod et al., 2006). Pharmaceutical companies' demand for chitin is increasing since the discovery of chitosan-based slimming product and the development of chitosan-based scaffolds (Roberts, 2008). The available sources of chitin include crab, shrimp, or prawn shells, all of which have a high chitin content (Tharanathan and Kittur, 2003). Even though exoskeleton waste usually has a high chitin content, high levels of mineralization and interlayer hydrogen bonds make chitosan processing from shrimp or crab shells a relatively difficult process. As a result, chitin processing requires extreme conditions for mineral elimination and subsequent deproteination and deacetylation (Muzzarelli, 1973). In some cases, a bleaching process is necessary to eliminate the reddish appearance caused by carotenoids (Uragami and Tokura, 2006). Excessive use of chemicals in processing results in the high price of chitosan as well as release of chemicals into the environment. For example, the concentration of sodium hydroxide (NaOH) required for deacetylation is 40–50% mass/mass (w/w) with a temperature around 100°C (Santhosh et al., 2010).

Chitin is known to have metal chelating properties. The value of chitin in removing trace metals was investigated in both raw chitin biomass (An et al., 2001; Chui et al., 1996; Dahiya et al., 2008; Kim, 2003; Vijayaraghavan et al., 2005, 2006) and purified chitin (Barriada et al., 2007, 2008; Bhatnagar and Sillanpää, 2009; Boukhlifi and Bencheikh, 2000; Boukhlifi et al., 2001; Zuo et al., 2001). Chitin biosorbents were prepared in various forms but most typically as powder. However, it was later discovered that the crystalline structure of chitin powder with low porosity was the cause of low adsorption capacity. This has led to numerous modifications of chitin, such as pore optimization (Guibal et al., 1998), crosslinking (Ge and Huang, 2010; Krishnapriya and Kandaswamy, 2009; Machado et al., 2009), xanthation (Kim et al., 2006), acid treatment (Niu and Volesky, 2007), and conversion to dithiocarbamate (Hase et al., 1990; Terada and Kawamura, 1991). However, the low degree of conversion of chitin to dithiocarbamate resulted in only a small increase in its metal adsorption capacity when compared to pristine chitin.

The key factor limiting chitin modification is its poor solubility (Pillai et al., 2009). Chitin modifications are mostly conducted in heterogeneous systems (i.e., between solid chitin with liquid reagents) that result in a low degree of conversion (Zou and Khor, 2004). The recent discovery of calcium chloride-saturated methanol as a solvent for chitin may generate more research on chitin modification. However, the high degree of acetylation of

chitin limits modification only to the C₂ amine functional group. Compared to chitin, chitosan is a preferred material for chemical modification due to a higher amine content when the degree of deacetylation is 60% or higher (Guibal, 2004). The influence of the characteristics of chitosan (molecular weight, degree of deacetylation, and crystallinity) has been studied with reference to the sorption properties of metals such as Pt(IV) (Jaworska, Kula et al., 2003; Jaworska, Sakurai et al., 2003) and Mo(VI) (Milot et al., 1998) for a series of different chitin/chitosan materials.

The ineffectiveness of chitin in adsorbing metal ions is also due to the low content of functional groups such as amine, which are polar enough to form stable complexes with trace metals (Camci-Unal and Pohl, 2010). Apart from Fe(III) and Pb(II) ions, the metal uptake for chitin is lower than its deacetylated derivative, chitosan (Zhou et al., 2004).

CHITOSAN

The production of chitosan from chitin requires three reaction stages of acidic deproteination/demineralization, deacetylation and bleaching. Chitosan has a wide range of possible uses, from pharmaceutical materials to an environmentally friendly fungicide (Uragami and Tokura, 2006). The interaction between chitosan and transition metals for use in water treatment has also been examined (Muzzarelli, 1973; Rana et al., 2009; Rhazi et al., 2002a). In fact, chitosan can be used in wastewater treatment as a coagulant and metal adsorbent (Renault et al., 2009). Some chitosan materials have been manufactured as membranes for filtration and this process physically increased strength and adsorption capacity (Uragami and Tokura, 2006). Among other attributes, an increase in porosity could permit greater adsorption capacity. Chitosan can be also used in a dissolved state to recover metal ions by ultrafiltration assisted by complexation. The chitosan, dissolved in an acid solution, is mixed with the metal-bearing solution. After metal complexation the metal-loaded macromolecules are retained by semipermeable membranes (Carreón et al., 2010; Guibal, 2005; Kuncoro et al., 2005). The coagulant properties are related to the protonated amine group of chitosan that can act as a positive site that would adsorb negatively charged particles such as clay or even protein, producing large agglomerates with greater mass. These coagulates then flocculate and sink from waste water. Chitosan's ability to remove metal is due to the extensive network of amine and hydroxyl functional groups which works either by chemisorption or physisorption (Juang and Shao, 2002). Improving the number of metal adsorption sites as well as metal selectivity can be achieved by chemically modifying C₂ amine and/or C₆ hydroxyl functional groups in chitosan (Jayakumar et al., 2005).

The major problem concerning the use of chitosan as a metal adsorbent is its poor stability under acidic conditions. With the exception of sulfuric

TABLE 1. Chitosan solubility

Solvent	Solvent concentration (mol/L)	Chitosan solubility (g/L)	Source
Formic acid	0.1	1.5	Li et al., 2006
Acetic acid	1	50	Hamdine et al., 2005
Hydrochloric acid	0.25	50	
Lactic acid	0.50	50	
Malic acid	0.50	50	
Citric acid	0.50	50	

and phosphoric acids, chitosan has good solubility in monoprotic acids, such as hydrochloric acid (HCl), nitric acid, and formic acid, at pH values of less than 6.5 (Qin et al., 2006). As shown in Table 1, the solubility of chitosan even at a low acidic concentration limits its application in acidic wastewater. Chitosan based sorbent's solubility in acidic solution may cause a decrease in wastewater flow due to pore clogging during treatment (Guibal et al., 1998). Low pH of some wastewater sources may also cause dissolution of chitosan, resulting in loss of mass that could lead to structural failure of the chitosan adsorbent (Oshita et al., 2002). Furthermore, the reusability of spent chitosan sorbent may be limited due to solubility in most acidic leaching solutions. Therefore, in order to maximize the potential of chitosan as a metal adsorbent, chitosan structure has been modified to increase its pH stability without compromising its metal adsorption abilities.

MODIFICATION OF CHITIN/CHITOSAN FOR WASTEWATER REMEDIATION

Chitosan-based sorbents can be modified to selectively adsorb metals based on the relative compound stability of metal versus non-metal species (Gadd, 2009). Generally, most toxic trace metals are soft or borderline acids. These toxic metals are predicted to form stable compounds with functional groups classified as "soft bases" (Pearson, 1963). For example, sulfur-containing functional groups, such as thiol, are known to bind strongly with soft acids such as mercury (Wang et al., 2010a). Chemical grafting of chitosan introduces new functional groups with soft base character, and they are more able to form strong bonds with soft metals (Miretzky and Cirelli, 2009). Sulfur-containing functional groups tend to form strong coordination bonds with most trace metals and could improve metal removal selectivity (Cathell et al., 2008). A number of studies have been conducted on improving the metal adsorption capacity by grafting chitosan to sulfur-containing compounds thus enhancing the stability of the modified chitosan-metal complexes (Muzzarelli and Tanfani, 1982).

The strategies for introducing sulfur-containing functional groups into chitosan (Figure 2) are mainly based on a grafting technique based on chemical modification of the C₆ hydroxyl group or C₂ amine groups. These grafting techniques involve mainly condensation reactions. Other reactions have also been applied to the grafting techniques, for example, insertion of carbon disulfide (CS₂) to form dithiocarbamate or xanthate, and thiocarbamylation using thiocyanate salts to form thiourea. Subsequent studies of chitosan dithiocarbamate investigated include firstly, variations of potassium, sodium and calcium as counter ions (Humeres et al., 2002; Ren et al., 2003); and secondly, structural optimisation into crosslinked resins with focus on

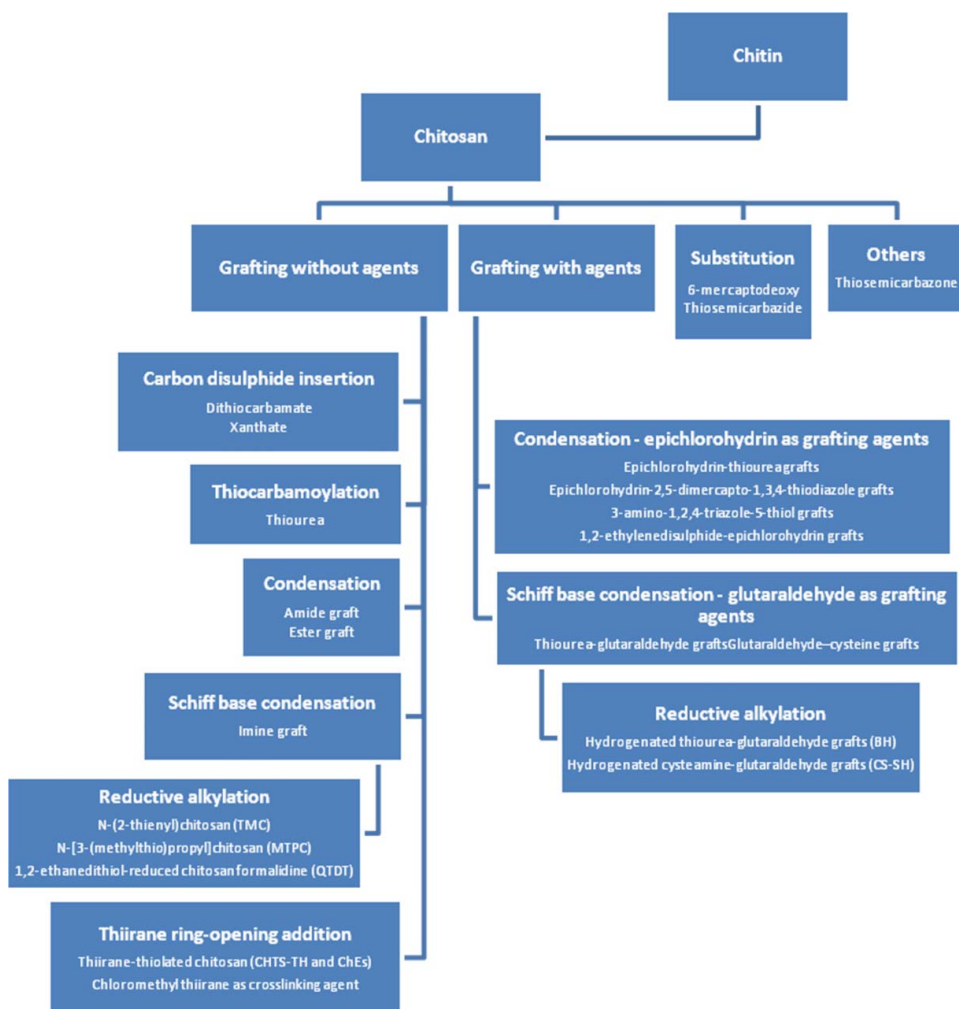


FIGURE 2. Approaches to sulfur chemical modifications of chitosan. (Color figure available online).

metals such as molybdenum, silver, mercury, bismuth, tungsten and tellurium (Mathur et al., 2000; Ninomiya et al., 2003; Oshita and Motomizu, 2004; Vieira and Beppu, 2006). Alternatively, xanthation of chitosan has been conducted with or without crosslinking (Alvarado-Monzon et al., 1996; Chauhan and Sankararamakrishnan, 2008; Kannamba et al., 2010; Sankararamakrishnan and Sanghi, 2006; Sankararamakrishnan et al., 2006, 2007, 2008).

The main method of grafting chitosan is by fusing graft molecules on to the chitosan polymer chain using the condensation reaction. This reaction forms amide, ester or imine bonds between chitosan and the grafted molecules (with production of by-products, such as water or hydrogen chloride). This approach to grafting of chitosan, however, is limited. A condensation reaction is only possible on C₂ amine and C₆ hydroxyl groups of chitosan, and only molecules with functional groups such as carboxyl, acyl halide, aldehyde or ketone can be grafted. However, molecules with primary amine groups such as cysteine and thiourea can be fused to chitosan using glutaraldehyde or epichlorohydrin as graft agents (Chassary et al., 2005; Merrifield et al., 2004). In addition, both glutaraldehyde and epichlorohydrin have been widely used as crosslinking agents to improve the durability of chitosan (Guibal et al., 1998). Besides these grafting techniques, several researchers chemically replaced C₆ hydroxyl groups using nucleophilic substitution. Tosyl chloride has been used together with other functionalized molecules such as alkyldiamines to increase the number of amine groups (Shimizu et al., 2007) or isothiuronium to replace the hydroxyl group with the thiol group (Kim et al., 1988).

Crosslinking of chitosan was introduced to increase the strength and decrease the solubility of the biopolymer in water, especially in acidic conditions (Tanuma et al., 2010). The stability of crosslinked chitosan is attributed to better structural resistance to changes under hydrated or acidic conditions. Crosslinking of chitosan was achieved using various crosslinking agents either by actions involving condensation or addition reactions. Recently, studies on the introduction of sulfur-containing molecules with both chelating as well as stabilizing capabilities have been reported (Sousa et al., 2009). In order to simultaneously enhance metal uptake selectivity and durability of chitosan, crosslinks with sulfur functional groups were introduced to the structure of chitosan. This approach was achieved by using mercaptosuccinic acid to form chitosan crosslinks by esterification. Recently, sulfur-containing crosslinking agents, such as thiiranes and 1, 2-ethanedithiol, have been used to simultaneously introduce the sulfur element and crosslinks to the polymeric chitosan chain (Zhang et al., 2006). Other methods of grafting include reduction on the Schiff base-grafted chitosan (Baba and Inoue, 1997; Baba et al., 1994, 1996, 1998).

Carbon Disulfide Insertion

DITHIOCARBAMATE

The chitosan dithiocarbamate derivative was first synthesized by Muzzarelli and Tanfani (1982) with a sulfur content of 2.4 mmol/g. Similarly, Humeres et al. (2002) reported a sulfur content of 2.2 mmol/g for potassium containing chitosan dithiocarbamate. Chitosan is more appropriate than chitin for dithiocarbamate synthesis due to the large fraction of amine groups in the former. The synthesis of the dithiocarbamate derivative of chitosan is achieved by adding carbon disulfide (CS_2) dissolved in alcohol. The reaction pathway of the CS_2 insertion of chitosan is shown in Figure 3. The optimum reaction pH for CS_2 insertion is in the range pH 7–8. This mild alkaline condition is usually achieved by adding a small amount of alkali such as ammonium hydroxide, tetramethylammonium hydroxide, NaOH, potassium hydroxide or a combination of potassium bicarbonate-potassium carbonate. However, strong alkali such as concentrated ammonia may also be used during dithiocarbamate modification of chitosan (Muzzarelli et al., 1982). The available cations (resulting from alkaline solution), such as sodium, potassium or ammonium, help in the stabilization of dithiocarbamic acid.

Dithiocarbamate derivative is known to be unstable at low pH and high temperature especially in the absence of metals of soft and borderline acid character (Hogarth, 2005). Acidic decomposition converts dithiocarbamate to corresponding amines when CS_2 is released (Humeres et al., 1998). However, to date, investigations into the pH stability of either chitin or chitosan dithiocarbamate ligand have not been reported. Most CS_2 insertion reactions on chitosan have been conducted at room temperature. In this case, the dithiocarbamate moiety, especially when grafted onto the primary amine, is susceptible to thermal decomposition (Sharma, 1986). The thermal decomposition of chitosan dithiocarbamate into isothiocyanate derivatives has not been reported so far. However, some reports have indicated that chitosan dithiocarbamate may decompose further to form thiourea. Humeres et al. (2002) studied the solid state ^{13}C nuclear magnetic resonance spectroscopy (NMR) spectra of chitosan dithiocarbamate and described the presence of thiourea derivatives. Recently, chitosan gels with thiocarbamoyl derivatives

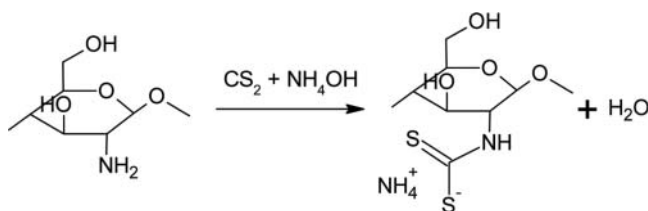


FIGURE 3. Carbon disulfide insertion of chitosan.

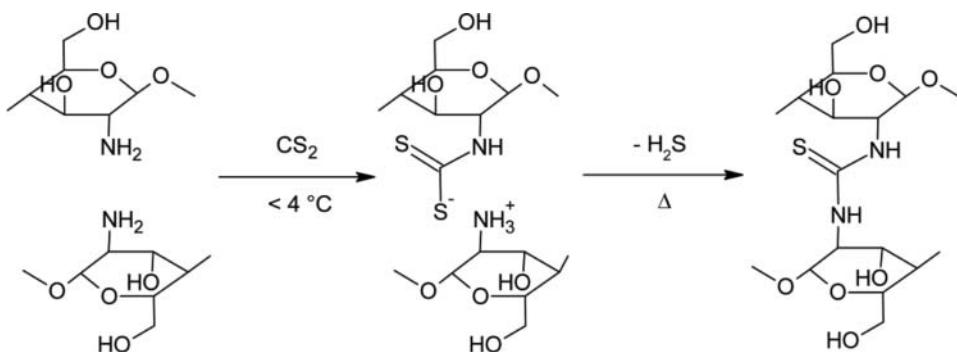


FIGURE 4. Two-step decomposition pathway of chitosan dithiocarbamate.

were synthesized by heating isothiocyanate salts with chitosan (Butewicz et al., 2010; Pestov et al., 2010). Decomposition of chitosan dithiocarbamate may have begun with the elimination of hydrogen sulfide to form isothiocyanate whereupon further reaction with another primary amine of chitosan forms thiourea crosslinks (Cookson and Beer, 2007). The two-step decomposition pathway of chitosan dithiocarbamate is shown in Figure 4.

The metal adsorption capacity of dithiocarbamate chitosan has been investigated for various metals (Table 2). It is found that dithiocarbamate derived from chitosan possesses generally had greater metal adsorption capacity than chitin dithiocarbamate. Metal adsorption studies on dithiocarbamate chitosan have been reported for Zn(II) (Mathur et al., 2000); Ag(I) (Asakawa et al., 2000); and Fe(II), Cu(II), Co(II), Ni(II), selenate (SeO_4^{2-}), and selenite (SeO_3^{2-}) (Pal and Bitterwolf, 2010). The suitability of chitosan dithiocarbamate as a wastewater treatment material depends on its physical stability during field application.

Other modifications include dodecanoic acid esterification on the C_6 hydroxyl group to modify the sorbent's hydrophobicity and subsequently, increasing solubility in the non-polar solvent (Inoue et al., 2001). However, in order to increase physical durability, crosslinking on hydroxyl groups has been carried out using several crosslinking agents, specifically epichlorohydrin (An, 2005) and ethylene glycol diglycidyl ether (EDGE). EDGE crosslinking of chitosan occurred at the C_6 hydroxyl after the amine groups were protected using benzaldehyde. Subsequent deprotection of amine using HCl removes benzaldehyde, which in turn enables the formation of a dithiocarbamate moiety via CS_2 insertion (Ninomiya et al., 2003).

In contrast to chitosan, chitin contains a larger proportion of acetylated amine with a primary amine content of 40% or less. Since CS_2 insertion is only possible on the primary amine, conversion to dithiocarbamate may be limited. The dithiocarbamate derivative of chitin was synthesized by Hase et al. (1990). The product of the reaction had a sulfur content of 0.22 mmol/g and 0.11 mmol/g of the nitrogen contained in chitin was successfully inserted

TABLE 2. Metal uptakes by dithiocarbamate derivatives of chitin and chitosan

Adsorbent	Crosslink	Metal	q_{\max} (mmol/g)	C_0	pH	Adsorption parameters	Source						
Chitin dithiocarbamate	Nil	Ag(I)	0.0374	5.0 mg/L (Breakthrough method with pack column at 1.0 mL/min)	—	<ul style="list-style-type: none"> • Sorbent amount: 0.4 g • Sulfur content: 0.22 mmol/g • Temperature: room 	Hase et al., 1990						
		Cd(II)	0.0044										
		Co(II)	0.0092										
		Cu(II)	0.0491										
		Fe(III)	0.0165										
		Ni(II)	0.0072										
		Au(III)	0.0640										
		Pd(II)	0.127										
		Chitosan dithiocarbamate	Nil					Cr(III)	0.77	0.5–10.0 mmol/L	6.8	<ul style="list-style-type: none"> • Sorbent amount: 0.3 g • Sulfur content: 0.1 mmol/g • Temperature: room • Sorbent amount: 100 mg • Sulfur content: 2.4 mmol/g (7.8%) 	Terada and Kawamura, 1991 Muzzarelli et al., 1982
								Mn(II)	0.15				
Co(II)	0.25												
Ni(II)	0.51												
Cu(II)	1.1												
Cd(II)	0.64												
Zn(II)	0.125												
Pb(II)	0.125												
Ag(I)	0.125												
Hg(II)	0.125												
<i>O,O'</i> -didecanoylchitosan dithiocarbamate	Nil	U(VI)	0.125	0.5 mmol/L (Volume: 25 mL)	5.0–7.0	<ul style="list-style-type: none"> • Sorbent dosage: 2.3 g/L kerosene • Temperature: 303 K 	Inoue et al., 2001						
		Cu(II)	Over 80%										
		Ni(II)											
		Fe(III)											
		Co(II)											
		Zn(II)											
		Chitosan dithiocarbamate (coated onto BaFe ₁₂ O ₁₉)	EPI					Au(III)	2.41	0.1 mol/L (Volume: 50 mL)	6.0	<ul style="list-style-type: none"> • Sulfur content: 1.6mmol/g (5.13%) • Sorbent amount: 100 mg 	An, 2005
								Pt(II)	0.78				
								Cu(II)	0.41				
								Ni(II)	0.05				

with CS₂. Even so, modification of chitin did not significantly improve its metal adsorption capacity. This was confirmed in the Pd(II) removal by chitin dithiocarbamate where the removal capacity at pH 4 did not exceed that of the unmodified chitin (5 μmol/g; Hase et al., 1990).

XANTHATE

In general, the xanthation reaction proceeds with a mechanism similar to the synthesis of chitosan dithiocarbamate where an ethanolic solution of CS₂ reacts with chitosan or chitin at high pH value and room temperature (Kim et al., 2006; Sankararamakrishnan et al., 2006). A high concentration of alkaline solution is often used during reaction (i.e., 25 mL of 3.5 M NaOH solution). The synthetic pathway of chitosan xanthation is shown in Figure 5. Sankararamakrishnan et al. (2006) crosslinked chitosan using glutaraldehyde to enhance its physical strength and perhaps, to limit the formation of dithiocarbamate by-product (by exhausting the amine groups). In contrast to the synthesis mechanism of dithiocarbamate, CS₂ is inserted onto the C₆ hydroxyl instead of the amine, creating an anionic moiety of xanthate. Insertion of carbon disulfide is possible on all available hydroxyl groups in chitosan, however, the C₆ hydroxyl group is favored due to little sterical hindrance (Schwaighofer et al., 2010).

The xanthation of chitosan was mostly conducted at room temperature (Sankararamakrishnan et al., 2006). In fact, the temperature requirement for xanthation differs to that for synthesizing chitosan dithiocarbamate. Similarly the xanthation of alkali cellulose to produce viscose has been conducted at an elevated reaction temperature (i.e., 30–45°C; Geyer and White, 1977). In fact, studies have suggested that a higher reaction temperature contributed to greater xanthate conversion (Kaller and Shanyuk, 1969; Rassolov and Finger, 1981).

Synthesis of chitin xanthate sorbent (crosslinked with epichlorohydrin) was first described in a patent (Stamberg et al., 1983). However, detailed reports on chitin or chitosan xanthate only appeared twenty years later, with the publication of a patent describing the synthesis of a non-crosslinked

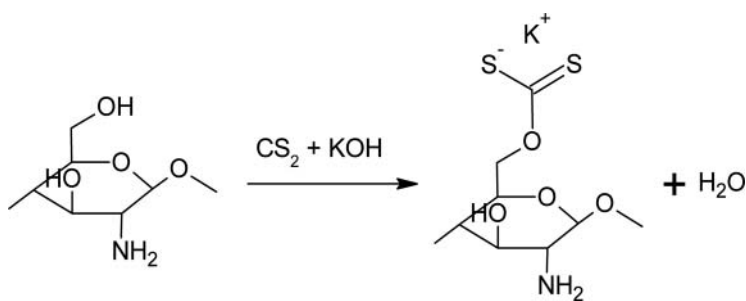


FIGURE 5. Xanthation of chitosan.

xanthate derivative of chitin and chitosan as a heavy metal scavenger for incinerator ash (Endo, 2003). Since these preliminary studies, research on both chitin and chitosan xanthate as a metal scavenger and adsorbent has intensified. Table 3 summarizes the maximum sorption capacities obtained for different metal ions using a series of xanthate derivatives of chitin/chitosan.

For example, Kim et al. (2006) prepared xanthated chitin by crosslinking with epichlorohydrin and examined its properties for Pb(II) sorption through sorption isotherms using the Langmuir equation: the maximum adsorption capacity (q_{\max}) rose to 1.41 mmol/g at 20°C and pH 4. However, it was not possible to determine the degree of conversion since the degree of deacetylation of chitin as well as the extent of xanthation on chitin were not discussed. Later, chitosan xanthation was extensively discussed by Sankararamakrishnan et al. (2006, 2007) with reference to the sorption of Cr(VI) and Cd(II), and by Chauhan and Sankararamakrishnan (2008) regarding the sorption of the Pb(II) ion. The method for xanthation was similar to the method described by Kim et al. (2006): chitosan hydrogel beads or flakes were crosslinked with glutaraldehyde prior to xanthation. More recently, Kannamba et al. (2010) used epichlorohydrin instead of glutaraldehyde to crosslink chitosan prior to xanthation of chitosan and the Cu(II) adsorption was determined at 0.4754 mmol/g at pH 5.0 and 30°C. The q_{\max} value of xanthated chitosan flakes for Cr(VI) was 1.4 mmol/g at pH 3 (Sankararamakrishnan and Sanghi, 2006); for Cd(II) was 3.177 mmol/g at pH 8 (Sankararamakrishnan et al., 2007) and for Pb(II) it was 1.557 mmol/g at pH 4 (Chauhan and Sankararamakrishnan, 2008). Despite the high q_{\max} value of xanthated chitosan flakes on sorption of Cr(VI), Cd(II), and Pb(II), the sulfur content of all xanthated chitin and chitosan was surprisingly not reported, except that Sankararamakrishnan et al. (2008) recorded 0.15 mmol/g of sulfur in xanthated chitosan. Despite the presence of sulfur as indicated by the results of energy-dispersive X-ray analysis (EDAX) and Fourier transform infrared spectroscopy (FTIR), the effects of sulfur content in xanthated chitin and chitosan on metal uptake cannot be clearly established from the data reported here.

THIOCARBAMOYLATION

Chitosan derivative with the thiocarbamoyl group is also referred to as thioamide or thiourea. It is synthesized by reaction between the amine of chitosan and ammonium isothiocyanate to produce chitosan isothiocyanate. Subsequent heating at over 70°C eliminates ammonia gas and isomerizes isothiocyanate to form thiocarbamoyl chitosan (Figure 6). Using this reaction, the sulfur content in the reaction product has been reported to be 0.2 mmol/g (Chen et al., 2005).

Thiocarbamoyl chitosan (Table 4) was also produced using chitosan, acidified with HCl in lithium isocyanate and subsequently heated to 50°C for 24 hr. The sulfur content of the resulting thiocarbamoyl chitosan was

TABLE 3. Metal uptakes of xanthate derivatives of chitin and chitosan

Adsorbent	Crosslink	Metal	q_{\max} (mmol/g)	C_0 (mg/L)	pH	Isotherm model	Adsorption parameters	Source
Chitin xanthate	Epichlorohydrin (EPI)	Pb(II)	1.41	10–30	4.0	Langmuir	<ul style="list-style-type: none"> • Temperature: 298.15 K 	Kim et al., 2006
Chitosan xanthate beads/flakes	Glutaraldehyde (GLU)	Cr(VI)	Flakes: 1.4 Beads: 4.931	50–1000	3.0	Langmuir	<ul style="list-style-type: none"> • Adsorbent amount: 10 mg • Room temperature 	Sankararamakrishnan et al., 2006
		Cd(II)	Flakes: 3.177	10–100	8.0		<ul style="list-style-type: none"> • Adsorbent amount: 50 mg 	Sankararamakrishnan et al., 2007
		Pb(II)	Flakes: 1.557	100–1500	4.0		<ul style="list-style-type: none"> • Adsorbent amount: 50 mg 	Chauhan and Sankararamakrishnan, 2008
	EPI	Cu(II)	Flakes at 30°C: 0.4754 50°C: 0.6841	10–100	5.0		<ul style="list-style-type: none"> • Room temperature • Adsorbent amount: 100 mg 	Kannamba et al., 2010
	Nil	Cr(III)	95.99%	100	7.5	Nil	<ul style="list-style-type: none"> • Temperature: 40°C 	Zhao et al., 2010

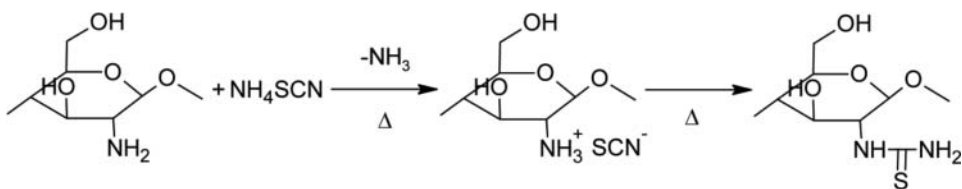


FIGURE 6. Thiocarbamylation of chitosan with ammonium thiocyanate.

0.934 mmol/g (Pestov et al., 2010). Recently, a greater degree of conversion to thiocarbamoyl chitosan was achieved by directly adding thiourea into the mixture of chitosan and ammonium thiocyanate. The converted thiocarbamoyl chitosan contained 2.65 mmol/g to 2.90 mmol/g sulfur (Butewicz et al., 2010; Gavilan et al., 2009).

Thiourea is a known metal sequestering agent with high binding ability (Murti and Khopkar, 1976; Zhang, Y. M. et al., 2006). Thus, various derivatives of thiocarbamoyl chitosan were synthesized to develop a metal adsorbent. Chitosan-based metal adsorbents with thiocarbamoyl substitutes (bearing alkyl, aralkyl, benzoyl, alkenyl, and aryl group) were synthesized and described in various patents (Baba and Noma, 2000; Hayasaka and Satake, 1995). For example, Donia et al. (2008) discussed the binding mechanisms of Hg(II) by bistiourea/thiourea/glutaraldehyde copolymers. Tautomer of thiourea exists in the form of thiol. A possible mechanism for removing mercury ion by thiocarbamoyl chitosan is shown in Figure 7, where coordination or chelation by two thiols is highlighted.

THIOL-CONTAINING GRAFTS BY CONDENSATION

Grafting of chitosan or chitin with carboxylic acid bearing at least one thiol/mercaptane group is possible by condensation (water molecules being released as a by-product). Typically, the reaction conditions for condensation are reflux at high temperature with the addition of concentrated sulfuric acid.

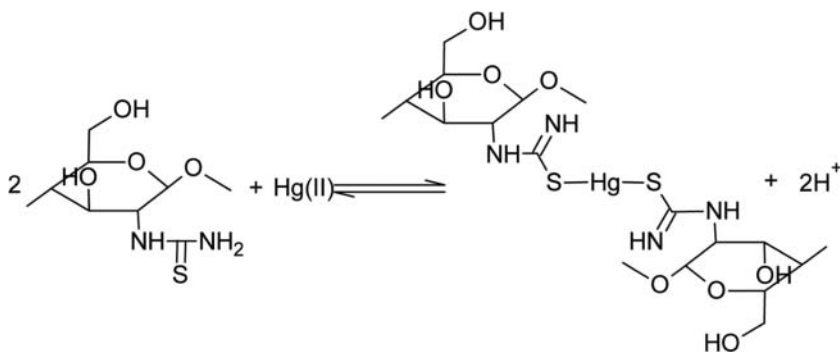


FIGURE 7. Proposed mechanism of Hg(II) removal by thiocarbamoyl chitosan.

Similar to chitosan xanthate/dithiocarbamate, successful grafting of organic molecules may not be just limited to one of either the amine or hydroxyl groups. When the amine and C₆ hydroxyl groups in chitosan are available, it is possible that a condensation reaction could simultaneously happen in at each functional group.

The first example of chitosan grafting by condensation employing mercaptosuccinic acid was reported by Lasko et al. (1993). The reaction pathway and the structure of chitosan condensate of mercaptosuccinic acid–chitosan (CHTS-MS) were hypothesized. However, crosslinking could have been formed due to lower solubility of modified chitosan in acidic media than pristine chitosan. Analysis of solid-state ¹³C NMR spectra suggested the formation of some new, but unspecified, carbonyl groups. However, based on the conditions and materials used, ester and/or amide derivatives may have been formed. Figure 8 shows the proposed reaction and structures of CHTS-MS. Lasko et al. (1993) evaluated the metal adsorption on CHTS-MS compared to unmodified chitosan at pH 5 (Lasko et al., 1993). While Cu(II) and Fe(II) adsorption of CHTS-MS did not improve in comparison to chitosan, adsorption of Cd(II) and Pb(II) improved two-fold and five-fold, respectively.

A similar approach to chitosan modification was employed by Yang et al. (2001) to graft thioglycolic acid to chitosan, yielding a sulfur content of 1.03 mmol/g. They evaluated the adsorption of several metal ions such as Ni(II), Cu(II), Cr(III), Cd(II) and Pb(II) using this modified chitosan. The highest uptake capacity was observed for Cd(II) with 1.669 mmol/g at pH 7. However, the structure of the chitosan condensates was not elucidated. Again, formation of bonds via the ester and amide groups was possible because concentrated sulfuric acid was used during the condensation reaction. The hydrolysis of ester and/or amide groups may occur in the presence of water, leading to a decrease in the grafting of sulfur compound. Cárdenas

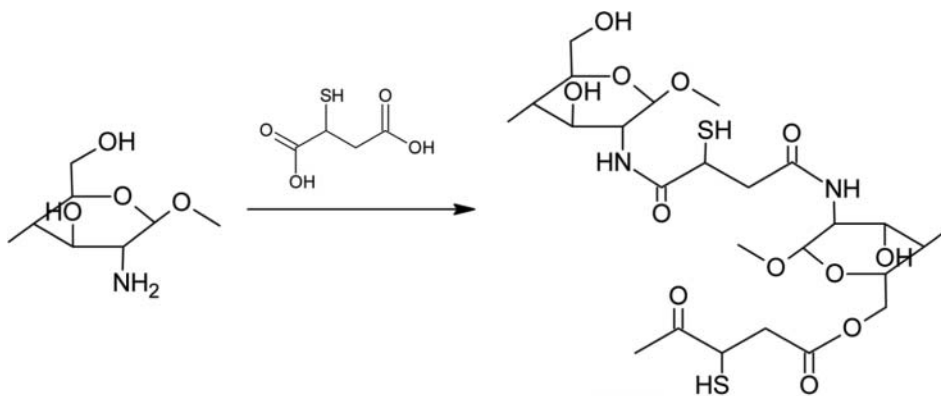


FIGURE 8. Synthesis of mercaptosuccinic acid derivatives of chitosan.

et al. (2001) then used a water-free synthetic route to graft thioglycolic acid to chitosan. Condensed water from successful grafting was constantly removed using the Dean-Stark apparatus with benzene as a solvent. As a result, a greater degree of conversion was achieved for chitosan having a sulfur content of 6.597 mmol/g. The existence of the thiol group in grafted chitosan was detected from a weak FTIR band of $\nu(\text{S-H})$ at 2558 cm^{-1} . Despite the high sulfur content, the metal uptake for Cu(II) and Hg(II) was not higher compared to other thioglycolic acid-grafted chitosan. The Langmuir maximum adsorption capacity was 2.05 mmol/g and 0.818 mmol/g for Cu(II) and Hg(II), respectively at pH 4.5.

In another approach to condensation, carbodiimide was considered as an activating agent that specifically targets condensation of the carboxyl group on the amine. In fact, selective grafting of cysteine and tryptophan on chitosan was attempted using cyclohexylcarbodiimide without success (Lasko et al., 1993). Recently, cysteine-grafted chitosan was synthesized and cast as thin films for qualitative metal detection where grafting of cysteine to chitosan was facilitated by *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC) (Cathell et al., 2008). Analysis of FTIR spectra of the grafted chitosans showed the formation of an amide derivative. The sulfur content was 0.572 mmol/g and 0.881 mmol/g for cysteine and thioglycolic acid-grafted chitosan, respectively. However, the grafted chitosan's metal uptake capacity was not determined. The reaction pathways for grafting cysteine and thioglycolic acid are described in Figure 9.

A different approach to selective grafting on the C₆ hydroxyl group on chitosan was conducted by Shimizu et al. (2007). They grafted functionalized molecules by substituting the C₆ hydroxyl group in the chitosan structure for the amine group. This strategy increased the number of amine groups in the chitosan structure for subsequent grafting of thiol-functionalized molecules. The C₆ hydroxyl group in the chitosan unit

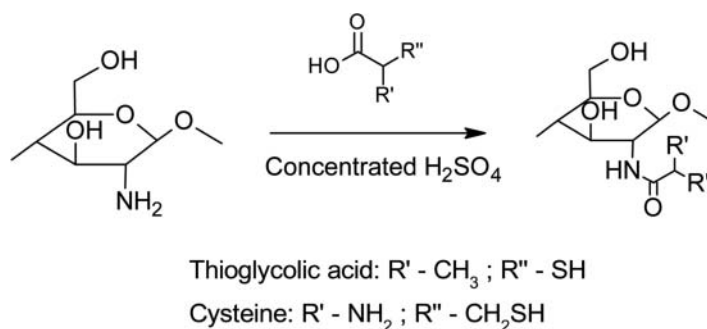


FIGURE 9. Grafting of thioglycolic acid and cysteine of chitosan by condensation.

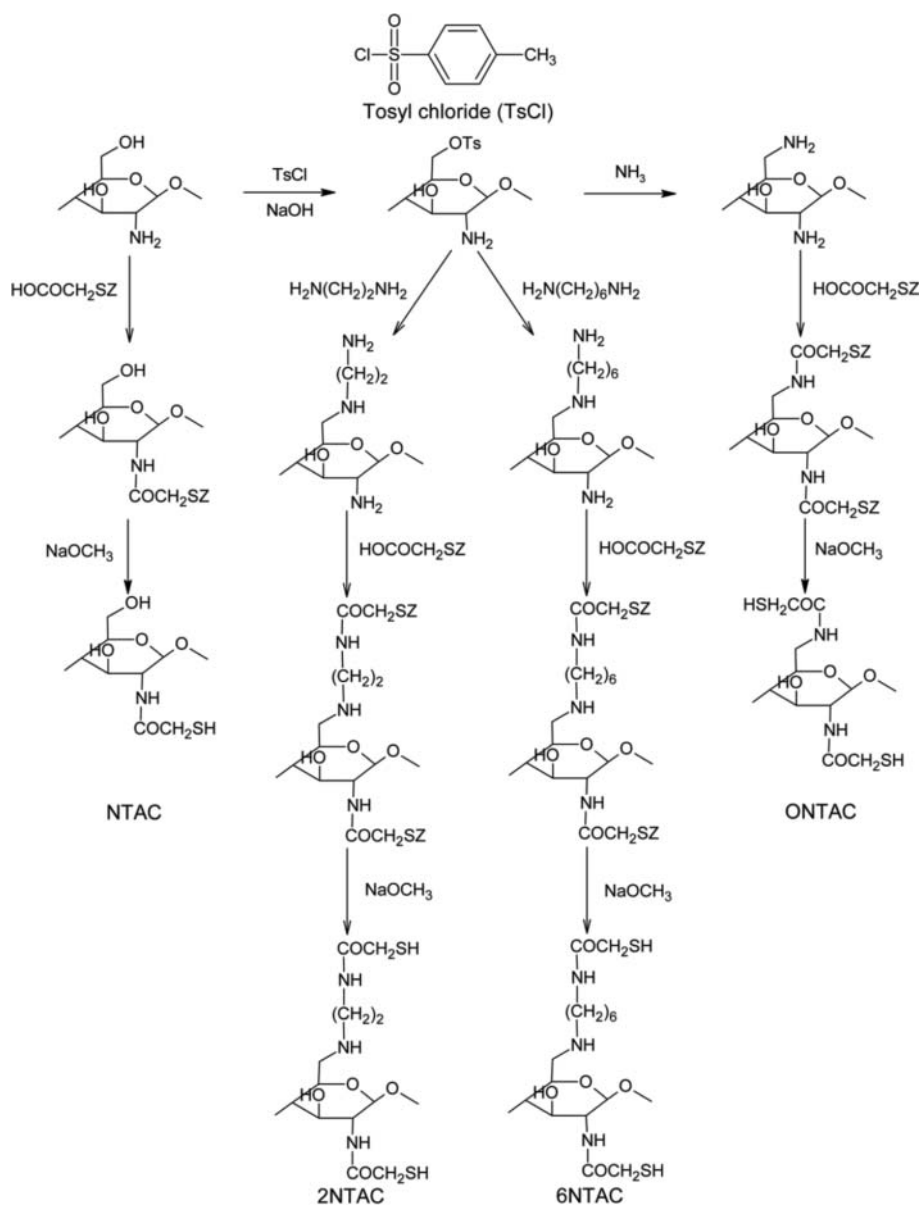


FIGURE 10. Synthetic pathway for amino(alkylamino)deoxychitosan and thiol derivatives.

was first modified to form tosyl chitosan (Figure 10). Then, further reaction of tosyl chitosan with ammonia or diamines eliminated the C₆ hydroxyl to give aminodeoxychitosan or aminoalkylaminodeoxychitosan. At this point, one to two new amine groups per unit chitosan were introduced. Condensation on C₂ amine and/or deoxyalkylamine on C₆ with

S-benzoyloxycarbonylmercaptoacetic acid (HOCOCH₂SZ) followed by hydrolysis with sodium methoxide introduced the thiol functional group to chitosan. With the earlier elimination of the C₆ hydroxyl, all grafts were amide derivatives. The synthesis pathway is shown in Figure 10. All modified chitosans, except aminodeoxychitosan (NTAC), bear two thiol groups. The amounts in thiol groups of the grafted chitosans were 2.28, 2.75, 3.09, and 4.07 mmol/g for NTAC, 2'-aminoethylaminodeoxychitosan (2NTAC), 6'-aminoethylaminodeoxychitosan (6NTAC), and O-amino-deoxychitosan (ONTAC), respectively. The Hg(II) uptake capacities at pH 6 for NTAC, 2NTAC, 6NTAC, and ONTAC were 0.56, 0.82, 1.00, and 1.40 mmol/g respectively. The amount of adsorbed Hg(II) ion increased with increasing thiol groups in grafted chitosan.

Other studies investigated the phytoremediation of metal contaminated soil assisted by sulfhydryl chitosan synthesized with cysteine or thioglycolic acid (Yang et al., 2006; Zhang et al., 2006, 2007). The metal uptakes of all ester and/or amide condensates of chitosan are summarized in Table 5.

SCHIFF BASE CONDENSATION-GLUTARALDEHYDE AS GRAFTING AGENTS

Thiourea-glutaraldehyde grafts. The use of glutaraldehyde as a crosslinking agent for chitosan has been popular due to the simplicity of Schiff base condensation. The mechanism of Schiff base condensation between thiourea and glutaraldehyde was described by Abd El-Ghaffar et al. (2009). Reaction between two C₂ primary amines with dialdehydes of glutaraldehyde forms a diimine crosslink. Using the same concept, molecules with both primary amine and thiol/thione groups can be added to form chitosan grafts. Guibal et al. (2000) used this idea to prepare thiourea-grafted chitosan (TGC) and found that Pt(IV) adsorption was proportionate to the amount of thiourea grafted to the chitosan sorbent (Table 6). This process was found to be little influenced by pH. The adsorption of Pt(IV) by TGC increased with the addition of chloride but decreased when sulfate ions were added. Consequently, the removal of Pt(IV) was enhanced by chloride complexation. The comparison of the sorption profiles in HCl and sulfuric acid (H₂SO₄) solutions by adding complementary anion (chloride anions with sulfuric acid solutions, and sulfate anions with HCl solutions) demonstrated: (a) the important contribution of metal speciation on the binding properties; and (b) the change in the sorption mechanism by grafting thiourea moieties. Indeed, in HCl solutions the addition of sulfate anions strongly decreased metal sorption with glutaraldehyde crosslinked chitosan while with the thiourea-grafted material the decrease in sorption capacity was limited. On the other hand, in sulfuric acid solutions, the addition of chloride anions slightly increased sorption properties (enhancing the formation of chloroanionic Pt(IV) ions that can bind to protonated amine groups of chitosan and to thiourea moieties). For the glutaraldehyde derivative of chitosan, this was prior to reducing sorption properties when the concentration of chloride

TABLE 4. Metal uptakes of thiocarbamoyl derivatives of chitosan

Adsorbent	Crosslink	Metal	q_{\max} (mmol/g)	C_0 (mg/L)	pH	Isotherm model	Adsorption parameters	Source
Crosslinked Cross-linked <i>N</i> -thioamido chitosan	Epichlorohydrin (EPI)	Cu(II)	82% (pH 3)	100	1–7	Nil	• Sulfur content: 1.65 mmol/g (5.27%)	Kim et al., 1988
		Cd(II)	28% (pH 5)					
		Pb(II)	72% (pH 6)					
		Hg(II)	100% (pH 2–7)					
		Cr(VI)	78% (pH 2)					
Thiocarbamoyl (S2) linked	Thioamide Glutaraldehyde (GLU) & thioamide	Hg(II)	pH7: 7.2037 pH5: 3.080	0–200	2, 5, 7	Langmuir	• Sorbent amount: 20 mg • Sulfur content (S2): 2.68 mmol/g (8.47%)	Gavilan et al., 2009
		U(VI)	89% (pH 5)					
		Pd(II)	pH7: 6.3373 pH5: 3.026					
		Pt(IV)	pH2: 2.293 $q_{m,1}$: 2.534 $q_{m,2}$: 2.122	Pd(II): 0–300 Pt(IV): 0–400	0.6 (0.25 mol/L HCl)	Langmuir (Bi-site model)	• Sorbent amount: 20 mg • Sulfur content (S1): 2.68 mmol/g (8.47%)	Butewicz et al., 2010
		Pd(II)	$q_{m,1}$: 1.131 $q_{m,2}$: 0.376					
Crosslinked thiocarbamoyl (SC1)	Thioamide GLU & thioamide	Pt(IV)	$q_{m,1}$: 2.479 $q_{m,2}$: 2.465					
		Pd(II)	$q_{m,1}$: 1.128 $q_{m,2}$: 0.327					
		Pt(IV)	0.490	Pt(IV): 115	2	Nil	• Sorbent amount: 10 mg TCC	Pestov et al., 2010
		Pd(II)	1.240	Pd(II): 47			• Sulfur content (TCC): 0.934 mmol/g (2.99%); (RDC): 1.64 mmol/g (5.24%)	
		Pt(IV)	1.120					
Thiocarbamoyl (RDC)	Thioamide	Pd(II)	2.470					

TABLE 5. Metal uptakes of amide and/or ester condensate of chitosan

Adsorbent	Metal	q_{\max} (mmol/g)	C_0 (mg/L)	pH	Isotherm model	Adsorption parameters	Source
Mercaptosuccinic acid	Cu(II)	0.46 (59%)	50 (Volume: 100 mL)	5.0	Nil	<ul style="list-style-type: none"> Sorbent amount: 100 mg Temperature: 298 K 	Lasko et al., 1993
	Cd(II)	0.12 (28%)					
	Pb(II)	0.065 (27%)					
Aminodeoxychitosan (NTAC)	Fe(III)	0.081 (9%)	0 to 28	6.0	Nil	<ul style="list-style-type: none"> Sorbent amount: 10 mg Amount of thiol (mmol/g): NTAC (2.28), 2NTAC (2.75), 6NTAC (3.09) and ONTAC (4.07) Temperature: 303 K 	Shimizu et al., 2007
	Hg(II)	0.56					
		0.82					
2'-aminoethylamino-deoxychitosan (2NTAC)		1.00					
		1.40					
6'-aminohexylamino-deoxychitosan (6NTAC)							
O-amino-deoxychitosan (ONTAC)							
Thioglycolic acid (S-chitosan)	Pb(II)	1.141	50	5.66.0	Nil (Column adsorption)	<ul style="list-style-type: none"> Sorbent amount: 1500 mg Sulfur content: 1.02 mmol/g (3.27%) 	Yang et al., 2000
	Cd(II)	1.386					
	Cu(II)	2.05	5-300	4.5	Langmuir	<ul style="list-style-type: none"> Sorbent amount: 100 mg Sulfur content: 6.597 mmol/g (21.11%) 	Cárdenas et al., 2001
	Hg(II)	0.818					
	Cu(II)	1.55	2500	7.0	Nil	<ul style="list-style-type: none"> Temperature: 293 K Sulfur content: 1.03 mmol/g (3.29%) 	Yang et al., 2001
	Cd(II)	1.669					
	Ni(II)	0.658					
	Pb(II)	1.141				<ul style="list-style-type: none"> Sorbent amount: 100.0 mg Temperature: 298 K 	
	Cr(III)	0.373					
				5.6			
				6.0			

anions exceeded 0.1 M (competition effect of chloride ions). With TGC, the same behavior was observed but the thiourea groups being less sensitive to chloride ions, the sorbent maintained high sorption capacities even at a high chloride concentration. When the glutaraldehyde derivative of chitosan binds Pt(IV) chloro-anions are produced by the ion exchange/electrostatic attraction mechanism (being sensitive to metal speciation and competition effect of anions), and the TGC binds Pt(IV) through complexation with sulfur groups. The reaction was less sensitive to metal speciation and the effect of competition. The early reaction of thiourea and glutaraldehyde may have produced imine conjugates with the aldehyde group on one side or both ends with the repeating unit (n) being greater than 1. Subsequent condensation of the imine conjugates to chitosan could produce a graft or crosslinks with both the imine and thiourea moieties (Figure 11).

A similar approach to grafting thiourea was adapted to synthesize thiourea modified *O*-carboxymethyl chitosan resin (TMCR) (Wang et al., 2010a; Wang et al., 2010c). The NaOH-swelled chitosan first reacted with chloroacetic acid to form *O*-carboxymethyl chitosan. Then, thiourea was grafted onto C₂ amine using glutaraldehyde. The reaction pathway is described in Figure 11. The sulfur content of TMCR resin was not reported by the authors, however, FTIR spectra analysis of the resulting TMCR resin showed two new chelating sites with a carboxyl group being introduced at the C₆ hydroxyl and a thiourea group at the C₂ amine. The q_{\max} for Hg(II)

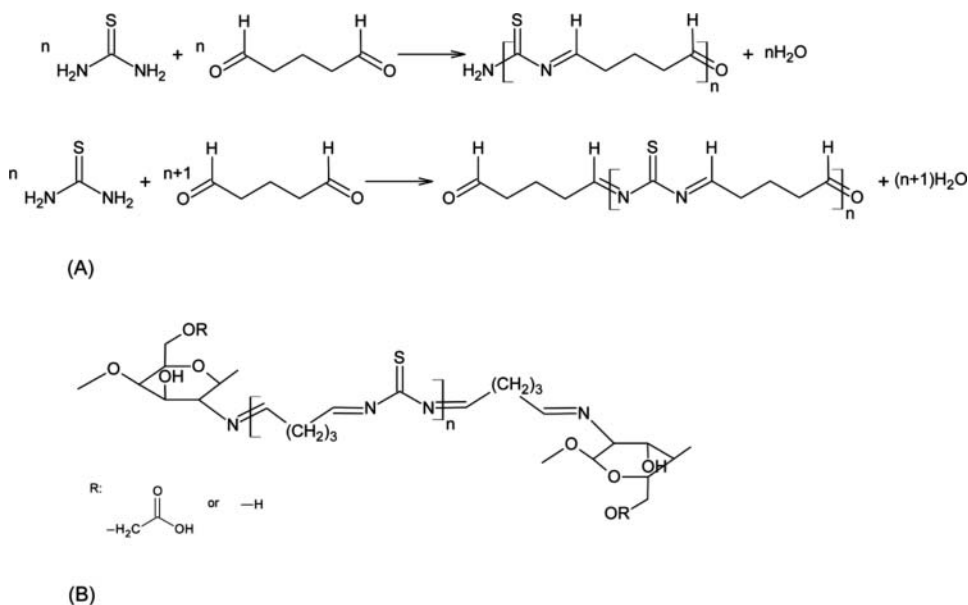


FIGURE 11. Schiff base condensation of thiourea with glutaraldehyde (A) and structure of thiourea grafted chitosan (B).

at pH 4.9 and Ag(I) at pH 4.0 were 6.23 and 3.81 mmol/g, respectively. In order to enhance adsorption selectivity of TMCR to Pb(II), *O*-carboxymethyl chitosan resin was templated with Pb(II) ions prior to the thiourea grafting process to create cavities. Compared to the non-Pb(II) templated TMCR, the Pb(II) adsorption capacity of the templated TMCR was improved by approximately 0.5 mmol/g. The adsorption of Pb(II) on templated TMCR was lower when other metal ions such as Cu(II), were present. However, the Pb(II)-templated-cavities' effect on Pb(II) adsorption selectivity was not discussed. A comparison study of Pb(II) adsorption in a binary metallic system between template and nontemplated TMCR resin may provide the necessary information to obtain a better mechanistic understanding of the sorption process.

Glutaraldehyde-cysteine grafts. Cysteine grafting of chitosan was achieved using glutaraldehyde as a grafting and crosslinking agent (Merrifield et al., 2004). Chitosan gel beads were first crosslinked with glutaraldehyde solution followed by the Schiff base condensation with cysteine to form imine grafts. The chemical structure and the sulfur content of cysteine-grafted chitosan gel beads were not discussed in detail in this study. However, based on the authors' synthesis process, chitosan may have been mainly crosslinked with glutaraldehyde. In fact, successful grafting of cysteine would rely on the amount of unreacted parts of the glutaraldehyde from an earlier crosslinking reaction with the possible formation of a disulfide bond between grafted cysteine (Figure 12). Nevertheless, deducing the chemical structure and the degree of conversion is not possible without chemical characterization of adsorbent gel beads, such as sulfur elemental analysis and infrared spectroscopy. Even with an inconclusive chemical structure, Hg(II) adsorption of cysteine-grafted chitosan beads improved to ca 2.7 mmol/g, compared to ca. 1.3 mmol/g by chitosan gel beads crosslinked with glutaraldehyde. The molar adsorption capacity of Hg(II) was approximately 8 mmol/g at pH 7.

CONDENSATION GRAFTING—EPICHLOROHYDRIN AS GRAFTING AGENTS

Epichlorohydrin-thiourea grafts. The method of using epichlorohydrin as a grafting agent for thiourea was first reported by Cárdenas et al. (2001) to synthesize *N*-(2-hydroxyl-3-mercaptopropyl)-chitosan derivative (Eq. 1). Similar chitosan derivatives were also synthesized and described as TDC (Chassary et al., 2005). Recently, a similar approach was used to synthesize xhitosan microsphere with epichlorohydrin-thiourea grafts (TCS) and magnetic chitosan microsphere with epichlorohydrin-thiourea (TMCS), where thiourea was grafted to the crosslinked chitosan microsphere and chitosan-coated magnetic ferrite particles (Zhou, Liu et al., 2009; Zhou, Wang et al., 2009). The synthesis pathways of (Eq. 1), TDC, TCS, and TMCS are shown in Figure 13. The reaction begins by adding epichlorohydrin for 36 hr followed by thiourea for another 12 hr. Subsequent hydrolysis using NaOH solution yields a thiol-bearing graft on the C₂ amine in chitosan (Eq. 1) with

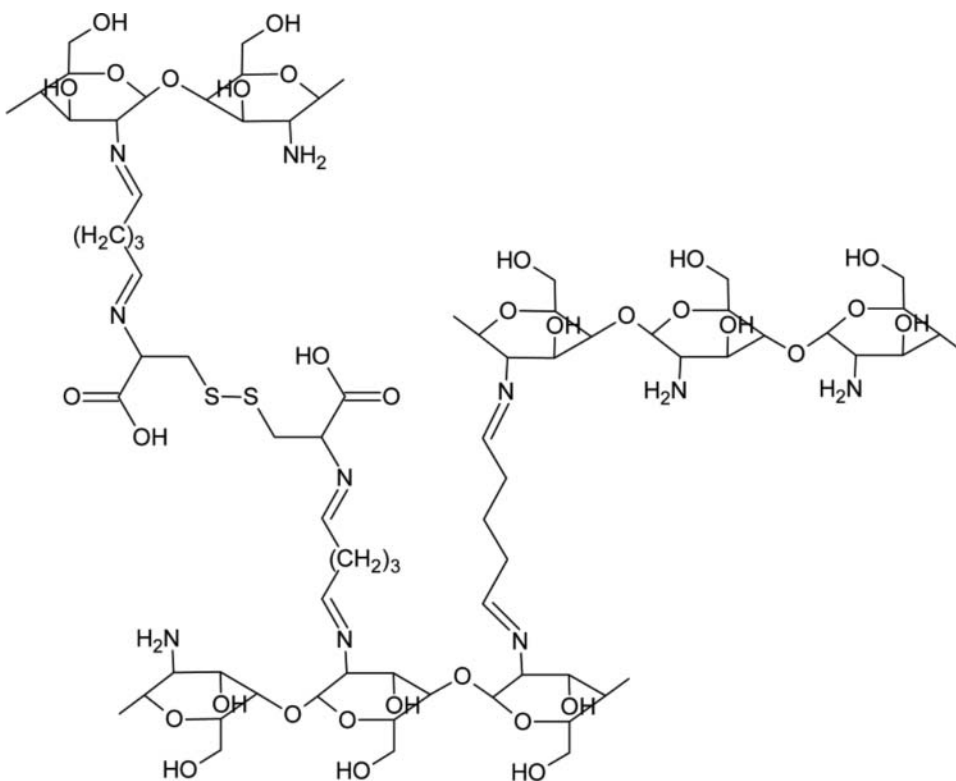


FIGURE 12. Proposed structure of cysteine-glutaraldehyde chitosan.

a sulfur content of 2.54 mmol/g. A similar synthesis method was employed by Chassary et al. (2005) to graft thiourea onto chitosan flakes to create TDC. They used a series of sorbents (glutaraldehyde crosslinked chitosan, polyethyleneimine-grafted chitosan, and a thiourea-grafted chitosan) for the sorption of Pd(II) and Pt(IV) from binary solutions both in batch and column systems. A marked preference of these sorbents for Pd(II) over Pt(IV) was observed, although this proved to be insufficient for selectively separating these metals. Pt(IV) was displaced from the sorbent by Pd(II) as evidenced by the appearance of overshoots on the breakthrough curves of Pt(IV) in the presence of Pd(II), while the presence of Pt(IV) did not significantly change

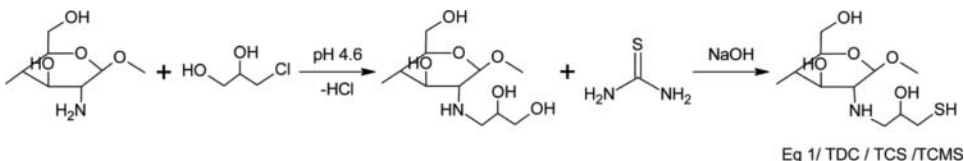


FIGURE 13. Thiourea grafting and subsequent hydrolysis of chitosan for Eq. 1, TDC, TCS, and TCMS.

the profiles of Pd(II) breakthrough. The sulfur contents of TCS and TMCS are 3.26 mmol/g and 2.12 mmol/g, respectively, while the sulfur content of TDC was not reported.

Compared to pristine chitosan, thiourea-grafted chitosan (*N*-(2-hydroxyl-3-mercaptopropyl)-chitosan or Eq. 1) exhibited improved metal uptake except for Cu(II) adsorption at pH 4.5 (Cárdenas et al., 2001). The q_{\max} value of Eq 1 for Cu(II) and Hg(II) was found to be 3.75 and 2.93 mmol/g, respectively. As for TMCS, the adsorption capacity for Cu(II) and Hg(II) was assessed to be 1.050 and 3.117 mmol/g, respectively. The thiourea-grafted-chitosan's metal uptake mechanism was first described by Cárdenas et al. (2001) who reported that 4 nitrogen ligands coordinated with Cu(II). However, when metal uptake occurs at low pH, the amine group is protonated and contributes to metal binding. Chassary et al. (2005) suggested that both electrostatic attraction by protonated amine and chelation by sulfur groups are involved in metal uptake mechanisms for Pd(II) and Pt(IV) at pH 2.

In another approach, phenylthiourea was grafted using epichlorohydrin at the C₆ hydroxyl of chitosan (Li and Yang, 2004). The reaction pathway is shown in Figure 14. The C₂ amine group of chitosan was first protected using benzaldehyde to form an alkali-stable imine group. Subsequent reaction of epichlorohydrin and phenylthiourea grafting occurred at the C₆ hydroxyl group of chitosan. Amine was then deprotected by mixing 4% HCl at room temperature for 2 days. The sulfur content of phenylthiourea-grafted chitosan was not reported. However, the presence of the thione group was indicated in FTIR spectra where a $\nu(\text{C}=\text{S})$ band was observed at 834 cm^{-1} . Metal uptake capacities of phenylthiourea-grafted chitosan were studied against pristine chitosan. The Cr(VI) uptake by grafted chitosan at pH 3 was 3.27 mmol/g,

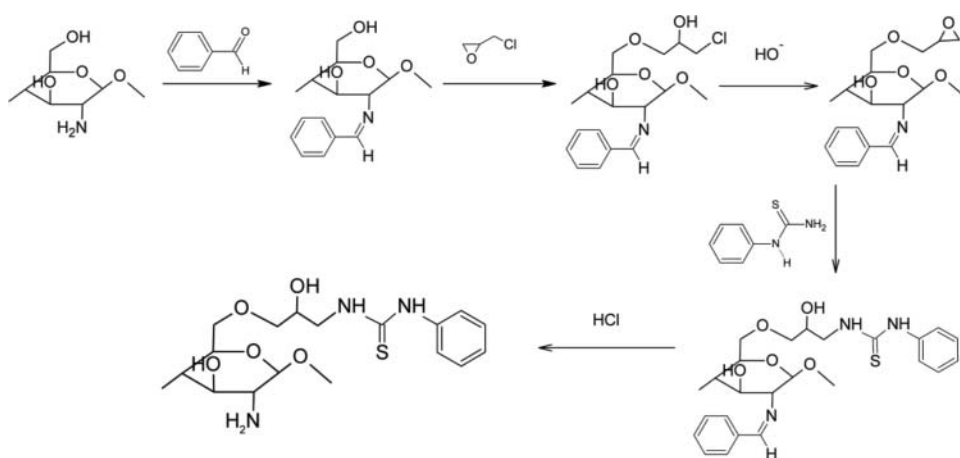


FIGURE 14. Phenylthiourea grafting by epichlorohydrin with amine protection.

which was higher than non-grafted chitosan (1.8 mmol/g). However, the Cu(II) uptake did not improve.

Epichlorohydrin-2,5-dimercapto-1,3,4-thiodiazole and 3-amino-1,2,4-triazole-5-thiol grafts. Azole (e.g., 3-amino-1,2,4-triazole) is a class of small molecules with five-member nitrogen heterocycles. Recently, an azole molecule containing a thiol functional group was grafted onto chitosan using epichlorohydrin as a grafting agent. Similarly, thiodiazole is another grafted molecule with sulfur and nitrogen elements in the five-member heterocycles. Owing to the abundance of nitrogen and sulfur elements, these molecules possess potential binding sites for metals and could be grafted onto chitosan to increase metal adsorption capacity. Atia (2005) grafted chitosan with 3-amino-1,2,4-triazole-5-thiol to create chitosan with epichlorohydrin-3-amino-1,2,4-triazole-5-thiol graft (CR-azole). Recently, Li et al. (2009) studied chitosan with epichlorohydrin 2,5-dimercapto-1,3,4-thiodiazole-grafted chitosan (CTS-DMTD) for adsorption of Au(III), Pd(II) and Pt(IV) ions. In each of these studies, chitosan was first crosslinked with glutaraldehyde. Then, epichlorohydrin was used as an agent to graft crosslinked chitosan. The synthesis pathway is shown in Figure 15. Most amine functional groups were likely to be converted into imine during crosslinking with glutaraldehyde. Thus, the availability of the amine group for epichlorohydrin grafting as suggested by the authors may be low with an estimated loss of 35–40% of the amine group (Guibal, 2004). Even so, chitosan grafting in the remaining C₂ amine may still be possible. Neither NaOH solution nor high reaction pH was used in these studies during grafting of chitosan, which otherwise may

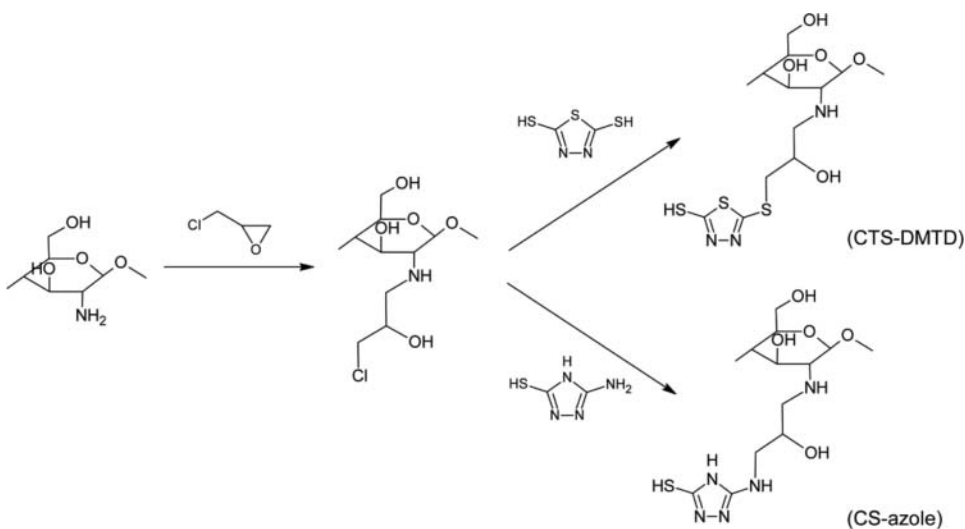


FIGURE 15. Chitosan grafting of 2,5-dimercapto-1,3,4-thiodiazole and 3-amino-1,2,4-triazole-5-thiol to using epichlorohydrin to produce CTS-DMTD and CS-azole.

cause epichlorohydrin to react with the C₆ hydroxyl group (Torres et al., 2007; Wan Ngah et al., 2008).

The reported sulfur content of CTS-DMTD was 1.46 mmol/g. The sulfur content of CR-azole was not reported. However, the estimated concentration of amine active sites of CR-azole was 6.4 mmol/g. The q_{\max} value of CTS-DMTD was 1.01, 0.16, and 0.078 mmol/g, respectively, for Au(III), Pd(II) and Pt(IV), while the q_{\max} value of Hg(II) and U(VI) for CR-azole was 2.21 mmol/g at pH 5.1 and 1.60 mmol/g at pH 3.9.

1,2-ethylenedisulfide-epichlorohydrin grafts. The role of epichlorohydrin in modification of chitosan is mostly related to its ability to act as a crosslinking agent or as a linkage to graft a small molecule. Except for the work of Guibal et al. (2000), Lasko et al. (1993), and Wang et al. (2010), no other such chitosan modification had been done, incorporating crosslinking and sulfur enrichment simultaneously. Recently, epichlorohydrin and 1,2-ethylenedisulfide were used to simultaneously incorporate sulfur into crosslinks of porous chitosan microspheres (EDSC; Kanai et al., 2008). The EDSC microspheres have large pores offering a higher metal sorption rate. The approach to EDSC synthesis is shown in Figure 16. A highly porous chitosan microsphere (HPCM) was first prepared via chitosan oil-in-water-in-oil (O/W/O) emulsion, followed by heterogeneous reaction with epichlorohydrin and 1,2-ethylenedisulfide. Unlike the TGC prepared by Guibal et al. (2000), synthesis of EDSC converts C₂ primary amine to secondary amine. Kanai et al. (2008) produced EDSC with a sulfur content of 1.84 mmol/g and q_{\max} value for Pd(II) adsorption (in 0.1 M HCl) of 2.33 mmol/g. Even though metal chelation was suggested as the adsorption mechanism for EDSC, the role of secondary amine and sulfide to the proposed adsorption mechanism was not considered.

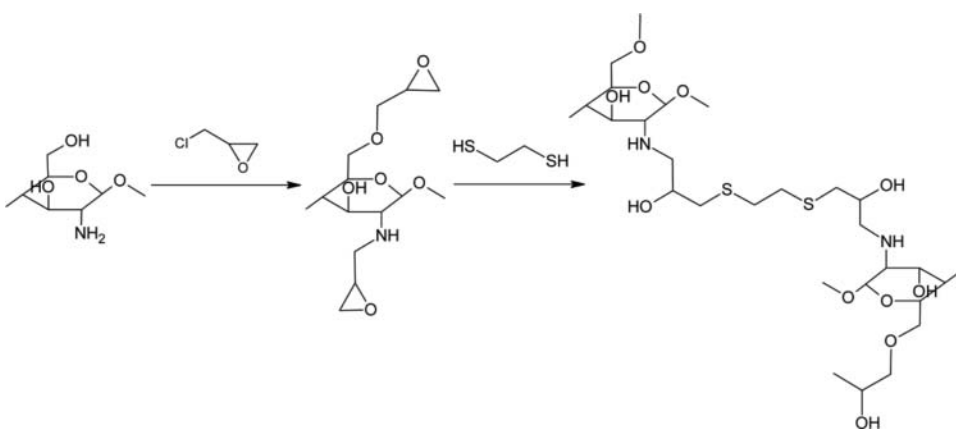


FIGURE 16. Chitosan grafting of 1,2-ethylenedisulfide using epichlorohydrin to produce EDSC.

REDUCTIVE ALKYLATION

Reductive alkylation, also known as reductive amination, is another approach to chitosan grafting. The process involves initial reaction between primary amine and ketone/aldehyde to form imine derivatives by Schiff base condensation. Following this, a subsequent reduction of imine results in a secondary amine. By using sulfur-containing ketones or aldehydes, introduction of a sulfur-containing functional group to chitosan is possible.

N-(2-thienyl)chitosan and *N*-[3-(methylthio)propyl]chitosan (MTPC). The first description of reductive alkylation on chitosan was the synthesis of *N*-(2-thienyl)chitosan (TMC) and *N*-[3-(methylthio)propyl]chitosan (MTPC; Baba et al., 1994). Figure 17 depicts the initial protection of the C₂ amine via Schiff base condensation to ensure subsequent crosslinking by epichlorohydrin on the C₆ hydroxyl. The final step of imine reduction using sodium borohydride in nitrogen atmosphere formed the secondary amine. This synthesis approach offered improved graft stability. The imine group, which is more susceptible to acidic hydrolysis was converted to a more stable amine group with simultaneous introduction of sulfur to the chitosan structure.

Based on elemental analysis, the degree of substitution of both *N*-(2-thienyl)chitosan (TMC) and MTPC produced by Baba et al. (1994) was more than 0.90. Both TMC and MTPC adsorbed Pd(II) ion in 0.01 M HCl with uptake capacities of 5.8 and 4.8 mmol/g, respectively. Compared to epichlorohydrin-crosslinked chitosan, Pd(II) uptake for both TMC and MTPC was about 2.5 to 3 times higher. The adsorption of Pd(II) was conducted in the presence of either HCl or ammonium chloride, which suggested that the adsorption mechanisms were through chelation and anionic exchange. The sulfide or thienyl group, as well as the protonated secondary amine, were chelated to the anionic PdCl₄²⁻ species. Similarly, chelation and cationic exchange mechanisms were proposed for Hg(II) adsorption by MTPC.

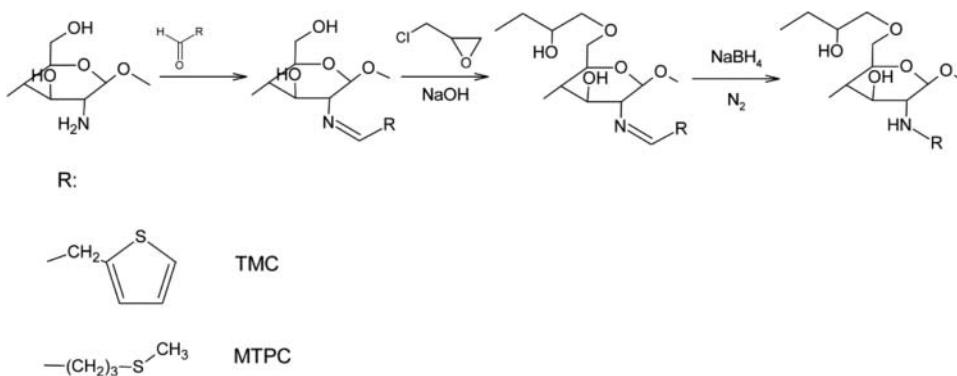


FIGURE 17. Synthesis of epichlorohydrin crosslinked *N*-(2-thienyl)chitosan (TMC) and *N*-[3-(methylthio)propyl]chitosan (MTPC).

Hydrogenated thiourea-glutaraldehyde grafts (BH). This approach to reductive alkylation is used to prepare samples of chitosan with hydrogenated thiourea-glutaraldehyde graft (BH), which is the chemically reduced form of TGC as discussed earlier. The thiourea-grafted chitosan is reduced by sodium borohydride, converting the imine group to the secondary amine (Ruiz et al., 2002, 2003). This reduction is expected to increase the compound's stability and to potentially make available new amine groups for metal binding. Figure 18 shows the possible structure of BH. Neither sulfur content nor the degree of conversion of BH was reported in the above studies. Furthermore the chemical structure of BH was not elucidated. However, based on the synthetic procedure given by the authors, the thione group may have been reduced to form thiol (Zhang et al., 1995). This claim, however, needs to be studied further using proper chemical characterization. The metal adsorption capacity of 3:2:1 BH (corresponding to optimum molar ratio between chitosan, thiourea and glutaraldehyde) for Pt(IV), Pd(II), Os(VI), and Ir(III) at pH 2.0 was 1.95, 3.10, 3.26, and ca. 1 mmol/g, respectively. The effect of thiourea grafting to chitosan on metal uptake capacity was different for Pd(II) and Pt(IV). The Pd(II) adsorption capacity was improved from 2.50 to 3.10 mmol/g, while Pt(IV) adsorption decreased from 2.05 to 1.95 mmol/g. Hydrogenation of thiourea-grafted chitosan did not affect metal adsorption capacity. This may indicate that the chemical change from imine to the secondary amine group did not significantly change the

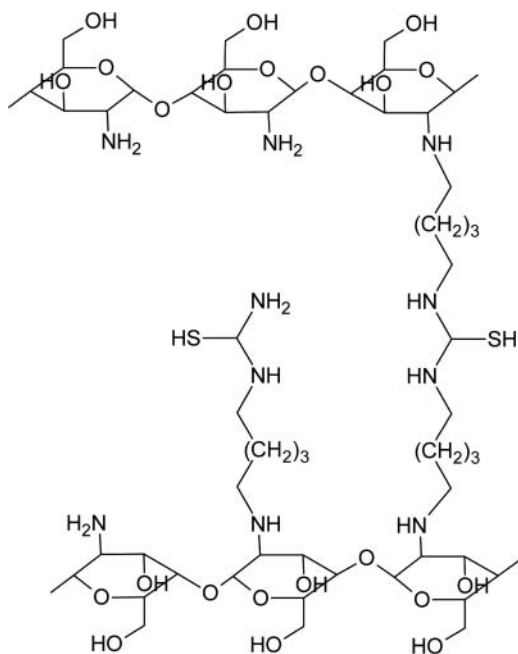


FIGURE 18. Possible structure of thiourea grafted and reduced chitosan (BH).

affinity of Pd(II) and Pt(IV) metals. This probably means that the sorption occurs by complexation on sulfur independently of the structure of nitrogen groups. When amine groups are involved in Pd(II) or Pt(IV) sorption, the crosslinking of chitosan did not significantly affect metal sorption; the ion exchange/electrostatic attraction mechanism is not inhibited by the steric hindrance around nitrogen, and the protonation of amine groups (even engaged in reaction with glutaraldehyde) is not significantly affected (Ruiz et al., 2000). Poor metal adsorption capacity of BH was also reported by Ruiz et al. (2003) for rhodium, rhenium, ruthenium, osmium, and iridium.

1,2-ethanedithiol-reduced chitosan formalidine (QTDT). Sulfur containing 1,2-ethanedithiol was immobilized on chitosan to study the adsorption of Ag(I), Hg(II), and Cu(II) (Vieira et al., 2005). This synthetic approach regarding 1,2-ethanedithiol-reduced chitosan formalidine (QTDT) was, to our knowledge, the first report of simultaneous crosslinking and sulfur enrichment since Lasko et al. (1993). The synthesis pathway for QTDT is shown in Figure 19. The thiol group (-SH) not only serves as a potent coordinating site for metal adsorption but also as a reducing agent. Epichlorohydrin crosslinked chitosan was first reacted with formaldehyde to convert the C₂ amine group into imine by Schiff base condensation. Subsequent reduction by 1,2-ethanedithiol would saturate the imine group to form the secondary amine. This resulted in the formation of a ethylenedisulfide crosslink connecting secondary amines from two different chitosan polymer chains. Immobilisation of 1,2-ethanedithiol to chitosan was successful with a sulfur content of 2.54 mmol/g.

The q_{\max} values of QTDT for Hg(II), Ag(I), and Cu(II) at pH 6.0 were 0.518, 0.540, and 0.244 mmol/g, respectively. Based on the q_{\max} values of

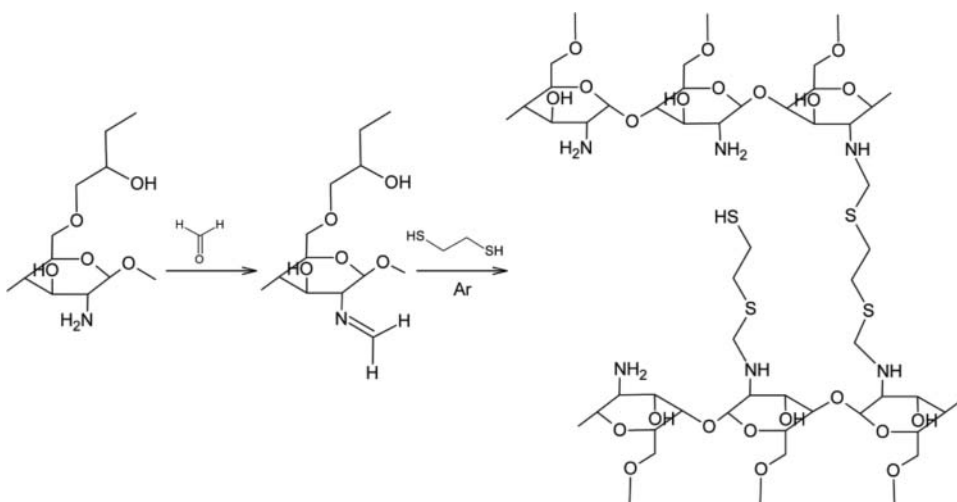


FIGURE 19. Synthesis of chitosan derivative of 1,2-ethanedithiol (QTDT).

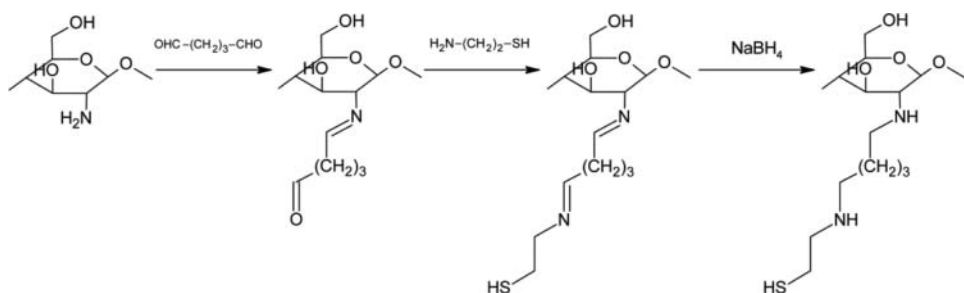


FIGURE 20. Synthesis of thiol functionalized chitosan (CS-SH).

QTDT, the calculated fractions of immobilized 1,2-ethanedithiol available for adsorption of Hg(II), Ag(I), and Cu(II) were 21.3%, 20.4%, and 9.6%, respectively.

Hydrogenated cysteamine-glutaraldehyde grafts (CS-SH). The synthesis of a thiol functionalized chitosan (chitosan with hydrogenated cysteamine-glutaraldehyde graft [CS-SH]) was performed in three steps using cysteamine and glutaraldehyde following the procedure shown in Figure 20 (Deng et al., 2010). The reaction began with the introduction of glutaraldehyde as an anchoring agent followed by grafting of cysteamine via Schiff base condensation to form imine groups. Subsequent chemical reduction with sodium borohydride turned imine into amine groups. During this reaction, the authors used a higher molar ratio of glutaraldehyde to chitosan to ensure that only one of the two aldehyde groups of glutaraldehyde reacted with chitosan. The newly introduced thiol groups in CS-SH were characterized by FTIR spectroscopy, in which two bands at 580 cm^{-1} and 1640 cm^{-1} were observed. The synthesized CS-SH material was only used as a coating film for Hg(II) electrochemical determination. The saturated Hg(II) uptake capacity of a 6.0 kHz CS-SH film was 2.09 mmol/g, determined by the quartz crystal microbalance technique.

THIIRANE RING-OPENING ADDITION—SIMULTANEOUS GRAFTING AND CROSSLINKING OF CHITOSAN

Thiirane—also known as ethylene sulfide—is a cyclic organosulfur molecule which readily reacts with amine to form thiol functional groups. Employing thiirane to enhance the sulfur-containing chelating group is suitable due to the abundance of amine groups in chitosan. Thiirane can be used to introduce a thiol group to the C₂ primary amine (Lasko et al., 1993; Sousa et al., 2009) or to serve as a crosslinking agent (Liu et al., 1996; Ni and Xu, 1996; Zhang et al., 2006).

Thiirane-thiolated chitosan (CHTS-TH and ChEs). Lasko et al. (1993) successfully used thiirane to introduce a new thiol group to chitosan with a degree of substitution of 0.27. To prevent polymerisation of thiirane, two

0.5 mL aliquots of thiirane were added daily to chitosan suspended in ethanol for two days. The structural change to thiolated chitosan (CHTS-TH) was characterized by FTIR and solid state ^{13}C NMR spectroscopic technique. A new peak observed at 32 ppm on NMR spectra of CHTS-TH indicated the presence of a methylene group of thiirane. The lower solubility of CHTS-TH in acidic media was not explained by the authors (Lasko et al. 1993). This may indicate the formation of a disulfide crosslink via oxidation of thiol groups from two adjacent chitosan chains. However, more characterization on CHTS-TH is needed to prove the existence of disulfide crosslinks. Metal adsorption of CHTS-TH was conducted with 50 mg/L of metal solutions at pH 5. The adsorption capacities for Cu(II), Cd(II), Pb(II), and Fe(II) were 9.3, 2.5, 1.3, and 1.6 mmol/g, respectively.

Recently, Sousa et al. (2009) employed a solvent-free approach in the reaction of chitosan with thiirane. The solid chitosan was added with excess liquid thiirane and stirred for 3 hr to form ethylenesulfide-grafted chitosan (ChEs). The unreacted thiirane in ChEs was eliminated by rinsing it with deionized water followed by drying at 55°C . The sulfur content of ChEs was 6.37 mmol/g. A weak shoulder at 2550 cm^{-1} observed in FTIR spectra of ChEs was assigned to the thiol group (-SH) and the appearance of new peaks at 30–50 ppm in ^{13}C NMR spectra were assigned to the methylene group derived from the thiirane. Based on the high sulfur content of ChEs, the authors proposed that two thiirane molecules reacted with one C_2 amine from the chitosan. The metal adsorption of ChEs for Cu(II), Co(II), Ni(II), and Zn(II) was evaluated using Langmuir isotherms and the q_{max} values were 1.73, 1.29, 1.34, and 0.90 mmol/g, respectively. The synthetic route for ChEs is shown in Figure 21.

Chloromethyl thiirane as crosslinking agent. The crosslinking mechanism of chloromethyl thiirane in chitosan is similar to epichlorohydrin due to their structural similarity. Chitosan crosslinking mechanisms of both chloromethyl thiirane and epichlorohydrin begin with a ring opening step followed by electrophilic addition of a chloromethyl thiirane molecule to either C_2 amine or C_6 hydroxyl (Ni and Xu, 1996; Sousa et al., 2009; Figure 21). Specific crosslinking at the C_6 hydroxyl group of chitosan can be conducted by initial protection of the C_2 amine group prior to crosslinking. This can be achieved via Schiff base condensation of amine using salicylaldehyde or

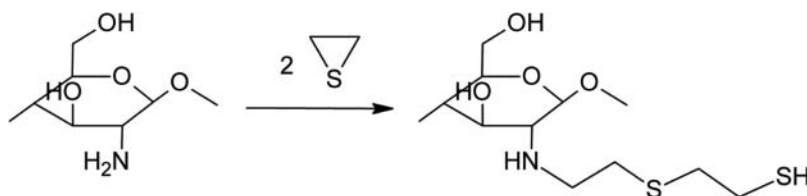


FIGURE 21. Synthesis pathway of ChEs and CHTS-TH.

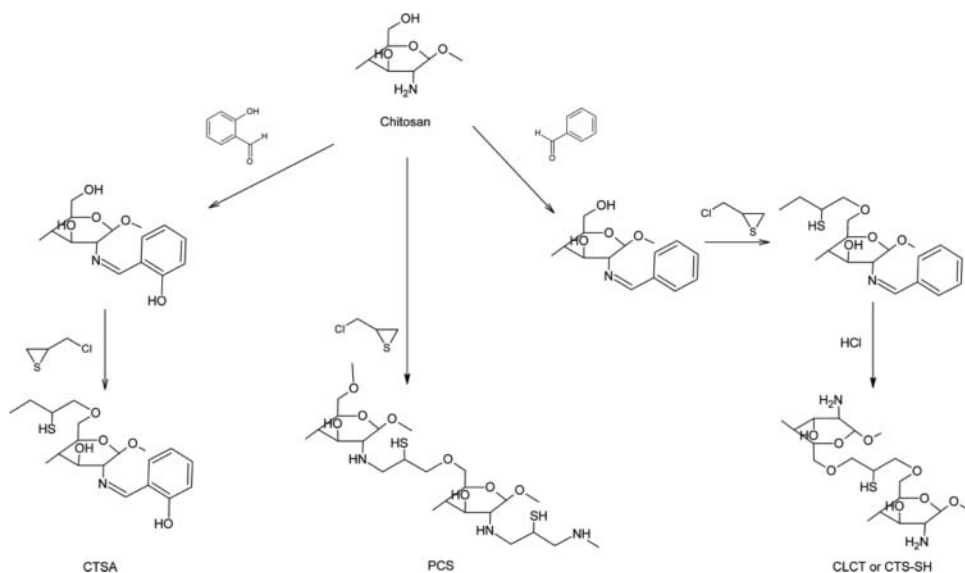


FIGURE 22. Synthesis pathways for CTSA, PCS, and CLCT/CTS-SH.

benzaldehyde which can be reversed by utilizing HCl hydrolysis (Liu et al., 1996). The synthesis pathway of chitosan crosslinking by chloromethyl thiirane (PCS) is shown in Figure 22.

Crosslinking chitosan with chloromethyl thiirane has the advantage of simultaneously introducing the thiol group. Chitosan resins crosslinked with chloromethyl thiirane or epichlorohydrin were first synthesized to investigate the metal adsorption of crosslinked chitosan resins (Ni and Xu, 1992). The adsorption capacities of chloromethyl thiirane crosslinked chitosan resins for soft metals such as Au(III), Pd(II), and Pt(IV) were higher than those of epichlorohydrin-crosslinked-chitosan resin. The resins of PCS were crosslinked at different ratios of chloromethyl thiirane and chitosan without the protection of C₂ amine. Thus, chitosan chains were bound to both C₆ hydroxyl and C₂ amine groups of chitosan. The sulfur content of PCS was proportional to the molar ratio of chloromethyl thiirane to chitosan. The highest sulfur content was in PCS₅ (synthesized with 10:1 mol ratio of chloromethyl thiirane and chitosan) with 7.547 mmol/g. The metal uptake of PCS resin increased as sulfur content rose (Table 9). The secondary amine was probably protonated at low pH, thus decreasing metal adsorption due to electrostatic repulsion. However, metal uptake of PCS resins at pH 5.6 decreased slightly with higher sulfur content.

Another chitosan crosslinking strategy aims to protect the C₂ amine so that the amines' function of coordinating metal is retained. This approach was first applied by Liu et al. (1996) to produce chloromethyl thiirane crosslinked chitosan (CLCT). However, CLCT only served as an intermediate in the synthesis pathway of the chitosan functional polymer-containing nitrile group

TABLE 6. Metal uptakes of grafted chitosan and O-carboxymethylated chitosan derivatives by Schiff base condensation of glutaraldehyde

Adsorbent	Crosslink	Metal	q_{\max} (mmol/g)	C_0 (mg/L)	pH	Isotherm model	Adsorption parameters	Source
Glutaraldehyde (GLU)-thiourea (TGC-3:2:1)	Nil	Pt(IV)	1.983 (H ₂ SO ₄) 1.775 (HCl)	20 15	2.0	Langmuir	• Sorbent amount: 10 mg	Guibal et al., 2000
GLU-thiourea (TGC-1:1:1)	Nil	Pd(II)	2.608 (293 K) 2.744 (313 K) 3.308 (293 K) 2.866 (313 K)	50.0 (constant)	2.0	Langmuir	• Sorbent amount: (5–30mg).	Guibal et al., 2002
GLU-rubeanic acid (RADC-PAM)	Nil	Hg(II)	6.2899	100.3–2507.4	4.9	Langmuir	• Sorbent amount: 2.0 g/L • Temperature: 299 ± 1 K.	Wang et al., 2010a
GLU-thiourea with O-carboxymethylated chitosan resin (TMCR)	Nil	Ag(I)	3.8118	ca. 53.9–1806.8	4.0	Langmuir	• Sorbent amount: 0.1 g • Temperature; 298 K	Wang et al., 2010c
Pb templated GLU-thiourea with O-carboxymethylated chitosan (resin)	Nil	Pb(II)	2.15	ca. 103.6–3418.8	6.0	Langmuir	• Sorbent amount: 0.1 g • Temperature: 298 K	Wang et al., 2010b
GLU-cysteine (gel beads)	GLU	Hg(II)	ca. 8	ca. 0–300.89	7.0	Freundlich	• Temperature: 298 K	Merrifield et al., 2004

Note. TGC = a:b:c, where a = volume of 50% glutaraldehyde (mL); b = mass of thiourea (g); c = mass of chitosan (g) in 20 mL of water.

TABLE 7. Metal uptakes of grafted chitosan using epichlorohydrin as grafting agent

Adsorbent	Crosslink	Metal	q_{\max} (mmol/g)	C_0 (mg/L)	pH	Isotherm model	Adsorption parameters	Source
Hydrolysed thiourea	Nil	Cu(II)	3.75 (pH 4.5)	10–104	2.5 & 4.5	Langmuir	<ul style="list-style-type: none"> • Sorbent amount: 100 mg • Temperature: 293 K 	Cárdenas et al., 2001
		Hg(II)	3.27 (pH 2.5) 2.93 (pH 4.5) 2.77 (pH 2.5)					
Hydrolysed thiourea (TMCS)	Glutaraldehyde (GLU)	Hg(II)	3.117	50–1500	5.0	Langmuir	<ul style="list-style-type: none"> • Sulfur content: 2.12 mmol/g • Sorbent amount: 30 mg at 1.5 g/L • Temperature: 301 K 	Zhou et al., 2009a
		Cu(II)	1.050	25–350				
		Ni(II)	0.2607	25–250				
Hydrolysed thiourea (TCS)	GLU	Pt(IV)	0.6659	10–400	2.0	Langmuir	<ul style="list-style-type: none"> • Sulfur content: 3.26 mmol/g • Sorbent amount: 100 mg at 3.33 g/L • Temperature: 298 K • Temperature: Room 	Zhou et al., 2009b
		Pd(II)	1.056					
Phenylthiourea	Nil	Cu(II)	1.2	?70	5.0	Nil		Li and Yang, 2004
2,5-dimercapto- 1,3,4- thiodiazole (CTS-DMTD)	GLU	Cr(VI)	3.27		3.0			
		Au(III)	1.008	0–43	Unknown	Langmuir	<ul style="list-style-type: none"> • Sulfur content: 1.46 mmol/g • Sorbent amount: 5 mg • Temperature: 288 ± 1 K 	Li et al., 2009
		Pd(II)	0.1595					
		Pt(IV)	0.07825					
3-amino-1,2,4- triazole-5-thiol (CR-azole)	GLU	Hg(II)	2.21	1–19	5.1	Langmuir	<ul style="list-style-type: none"> • Sorbent amount: 100 mg • Temperature: 303 ± 1 K 	Atia, 2005
		U(VI)	1.60	mM	3.9			
1,2-ethylene- disulphide (EDSC)	1,2-ethylene- disulphide- EPI	Pd(II)	2.33	106.42 (1 mmol/L)	0.1 M HCl	Langmuir	<ul style="list-style-type: none"> • Sulfur content: 1.84 mmol/g • Sorbent amount: 50 mg at 1.67 g/L • Temperature: 303 K 	Kanai et al., 2008

TABLE 8. Metal uptakes of reductive alkylated chitosan

Adsorbent	Crosslink	Metal	q_{\max} (mmol/g)	C_0 (mg/L)	pH	Isotherm model	Adsorption parameters	Source
<i>N</i> -(2-Thienyl)chitosan (TMC)	EPI	Pd(II)	5.8	0–70 mmol/L (Volume 20 mL)	0.01 mol/L	Nil	<ul style="list-style-type: none"> • Sorbent amount: 100 mg • Degree of substitution: > 0.9 • Temperature: 303 K 	Baba et al., 1994, 1996
			4.8					
<i>N</i> -[3-(methylthio)propyl]chitosan (MTPC)	EPI	Hg(II)	2.1	0–25 mmol/L (Volume 15 mL)	0.01 mol/L	Nil	<ul style="list-style-type: none"> • Sorbent amount: 100 mg • Degree of substitution: > 0.9 • Temperature: 303 K 	Baba et al., 1998
Hydrogenated GLU-thiourea (3:2:1 BH)	Nil	Pt(IV)	1.95	0–15 0–20 ca. 50 (const)	2.0	Unknown	<ul style="list-style-type: none"> • Temperature: 303 K • Temperature: room 	Ruiz et al., 2002, 2003
		Pd(II)	3.10					
1,2-ethanedithiol (QTDI)	EPI	Hg(II)	0.518	1.0–7.0 mmol/L (Volume: 3.0 mL)	6.0	Langmuir	<ul style="list-style-type: none"> • Sorbent amount: 50 mg • Sulfur content: 2.54 mmol/g • Temperature: 298.15 K 	Vieira et al., 2005
		Ag(I)	0.540					
		Cu(II)	0.244					
GLU-Cysteamine (CS-SH)	Nil	Hg(II)	2.09 ^a	14.5 mmol/L	1 mol/L HCl	QCM technique	<ul style="list-style-type: none"> • Sorbent amount: 10 µg • Temperature: 298.15 K 	Deng et al., 2010

^a q_{\max} calculated from Sauerbrey equation.

TABLE 9. Metal uptakes of thiirane derivatives from chitosan

Adsorbent	Metal	q_{\max} (mmol/g)	C_0 (mg/L)	pH	Isotherm model	Adsorption parameters	Source
Thiirane (GHTS-TH)	Cu(II)	9.3 (59%)	50 (Volume: 100 mL)	5.0	Nil	<ul style="list-style-type: none"> • Sorbent amount: 100 mg • Degree of substitution: 0.27 • Temperature: 298 K 	Lasko et al., 1993
	Cd(II)	2.5 (28%)					
	Pb(II)	1.3 (27%)					
	Fe(II)	1.6 (9%)					
Thiirane (ChEs)	Cu(II)	1.73	7.0×10^{-4} – 7.0×10^{-3} mol/L (Volume: 10 mL)	Unknown	Langmuir	<ul style="list-style-type: none"> • Sulfur content: 6.37 mmol/g • Sorbent amount: 20 mg • Temperature: 298 ± 1 K 	Sousa et al., 2009
	Co(II)	1.29					
	Ni(II)	1.34					
	Zn(II)	0.90					
2-chloromethylthiirane (CTS-SH)	Hg(II)	97.6%	0.5 mmol/L [Volume: 25 mL for Hg(II); 50 mL for Pb(II)]	5.0	Nil	<ul style="list-style-type: none"> • Sorbent amount: 10 mg 	Zhang et al., 2006
	Pb(II)	94.7%					
2-chloromethylthiirane (PCS ₅)	Ag(I)	4.46	0.1 mol/L (0.01 M HCl)	5.6 5.0	Nil	<ul style="list-style-type: none"> • Sorbent amount: 250 mg (Ag), 25 mg (Au, Pd, Pt), 60 mg (Hg, Cu, Zn) 	Ni and Xu, 1996
	Au(III)	4.86					
	Pd(II)	3.51					
	Pt(IV)	1.87					
	Hg(II)	4.60					
	Cu(II)	(PCS ₁) 2.05					
	Zn(II)	(PCS ₁) 1.26 (PCS ₁)					

(CT-CN) and its metal adsorption was not analyzed (Liu et al., 1996). However, Liu et al. (1996) did synthesize chloromethyl thirane crosslinked chitosan (CTSA) using salicylaldehyde and protect the C₂ amine to create a salicylidene moiety. Deprotection of C₂ amine was not conducted because salicylidene is able to chelate metal ions (Cao et al., 2004). Chloromethyl thirane crosslinked chitosan was later synthesized by Zhang et al. (2006a) as CTS-SH and the metal adsorption capacities for Hg(II) and Pb(II) were 97.6% and 94.7%, respectively, using 50 mL of 0.5 mmol/L of initial metal nitrate solution and 10 mg of CTS-SH sorbent at pH 5.0 (Zhang et al., 2006). The metal uptakes for CTSA and CLCT were not documented.

SUBSTITUTION OF C₆ HYDROXYL

The strategies for sulfur enrichment of chitosan so far have been based on grafting of thiol functionalized molecules to the chitosan structure. The idea of changing existing functional groups in the chitosan structure into sulfur-containing functional groups has not been popular. To the best of our knowledge, only two reports on functional groups being converted into chitosan exist. Both Shimizu et al. (2007) and Kim et al. (1988) utilized nucleophilic substitution of the C₆ hydroxyl group to add the thiol group to the chitosan structure. Kim et al. (1988) reported chitosan conversion in the C₆ hydroxyl groups to form 6-mercaptodeoxy chitosan and thiosemicarbazide derivatives as well as their metal sorption studies on metals.

6-mercaptodeoxy chitosan. Numerous studies have been conducted to modify the C₆ hydroxyl group into mercaptodeoxy moiety. The first synthesis of deoxymercapto chitosan was reported using metal adsorption studies at different pH values (Kim et al., 1988). The synthetic pathway (Figure 23) utilized 6-chlorodeoxychitosan as the starting material where thiourea was alkylated to form isothiuronium salt. Subsequent hydrolysis with NaOH yielded 6-mercaptodeoxychitosan with a sulfur content of 1.94 mmol/g. The ability to remove metal was evaluated using 0.15 g of 6-mercaptodeoxychitosan, 25 mL of 100 mg/L metal solutions and an adsorption time of 48 hr. The optimum metal uptake was 68% for Pb(II) at pH 6, 100% for Hg(II) at pH 2.5, 99% for Cu(II) at pH 6, 94% for U(VI) at pH 4, and 84% for Cr(VI) at pH 3.

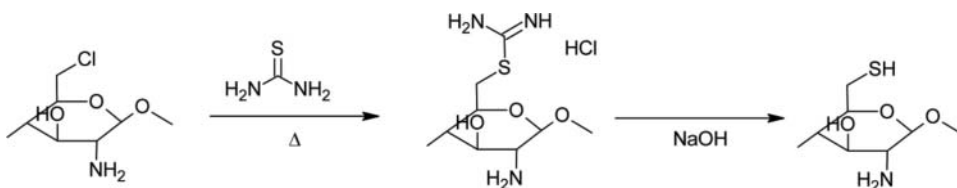


FIGURE 23. Synthesis of 6-deoxymercapto chitosan.

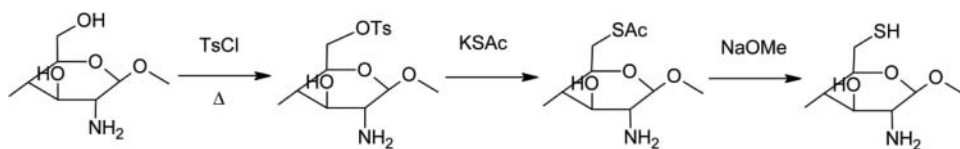


FIGURE 24. Synthesis of 6-deoxymercapto chitosan using tosy chloride (TsCl).

A different synthetic route for 6-mercaptodeoxychitosan was reported using tosyl chloride (Munro et al., 2009). As shown in Figure 24, the reaction begins with tosylation of chitosan followed by thiolation with potassium thioacetate (KSAC). Further reaction with sodium methoxide (NaOMe) yields 6-mercaptodeoxychitosan with a sulfur content of 2.3 mmol/g. This material, however, was not investigated for its metal adsorption properties.

Chitosan thiosemicarbazide. Chitosan derivatives of thiosemicarbazide were synthesized by Kim et al. (1988), and their metal [Cu(II), Cd(II), Pb(II), Hg(II), Cr(IV), and U(VI)] adsorption characteristics were also determined. The synthetic pathway shown in Figure 25 describes the effect of temperature on the reaction. The authors used a series of different reaction temperatures between 60°C and 158°C to synthesize thiocyanate chitosan. The highest sulfur content (2.17 mmol/g) was achieved at 120°C. Greater homogeneity of chitosan thiocyanate was obtained at a high reaction temperature. Subsequent addition of hydrazine yielded uniform chitosan thiosemicarbazide derivatives. The removal percentage of all metals, except Cr(VI) was proportional to the sulfur content of the resulting chitosan thiosemicarbazides. The ability to remove metal was evaluated using 0.15 g of chitosan thiosemicarbazides, 25 mL of 100 mg/L metal solutions and an adsorption time of 48 hr. Chitosan thiosemicarbazides with a sulfur content of 2.11 mmol/g were found to have the highest removal percentage with 72% for Cd(II), 87% for Pb(II), 100% for Hg(II), 88% for Cu(II), and 97% for U(VI) all at pH 4. Removal for Cr(VI) was reported as being 77% at pH 3.

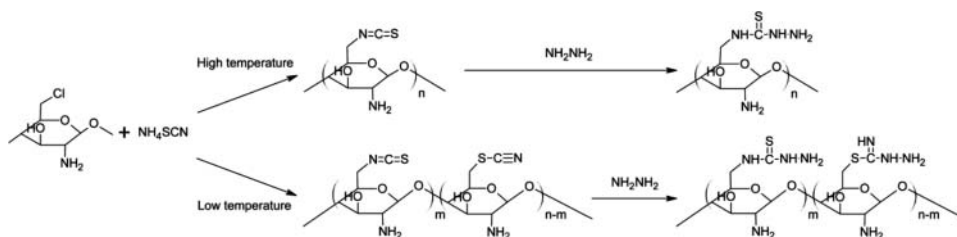


FIGURE 25. Synthesis pathways of chitosan thiosemicarbazide.

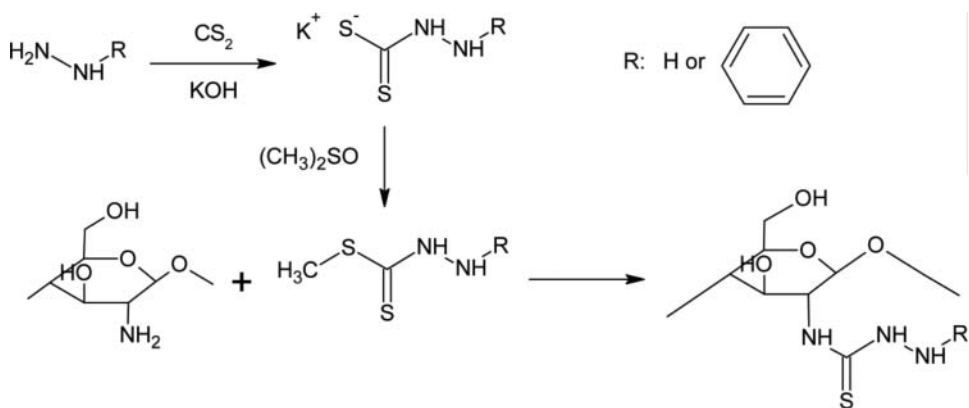


FIGURE 26. Synthesis pathway of 2-phenylhydrazine or hydrazine thiosemicarbazone chitosan.

OTHER APPROACHES TO SULFUR ENRICHMENT OF CHITOSAN–THIOSEMICARBAZONE DERIVATIVES

The chitosan thiosemicarbazone derivatives were synthesized by Zhong et al. (2010) to investigate their antioxidant activity. However, chelating activity may be related to antioxidant activity of chitosan derivatives and was subsequently determined. Fe(II) ions were used to compare the relative affinity of Fe(II) ions to pristine chitosan and chitosan thiosemicarbazone. The thiosemicarbazone derivative of chitosan was first prepared by reacting chitosan with hydrazine (or phenylhydrazine) thiocarboxylate at 100°C for 8 hr (Figure 26; Zhong et al., 2010). Initial preparation of hydrazine dithiocarboxylate was achieved by adding carbon disulfide drop-wise into a mixture of potassium hydroxide and hydrazine or phenylhydrazine cooled in an ice bath. The sulfur content varied between 2.51 mmol/g and 3.356 mmol/g. The q_{\max} value of chitosan thiosemicarbazone was not determined. However, Zhong et al. (2010) reported that the Fe(II) chelating activity of chitosan thiosemicarbazone was higher than that of the pristine chitosan. The authors attributed this improvement in sorption efficiency to the presence of both the amine (-NH-) and thione (C=S) groups in chitosan thiosemicarbazone.

CONCLUSION

Sulfur-containing functional groups have been introduced mainly by adding chemicals or condensation of organic molecules onto C₂ amine and/or C₆ hydroxyl groups of chitosan. Adsorption capacity of soft metals [i.e., Hg(II), Pt(IV), Pd(II), Au(I), Ag(I) and Cd(II)] is enhanced by the sulfur-incorporated

chitosan sorbent. However, this may not be the case for hard and borderline acid metals. For example, the Cu(II) (a borderline acid) adsorption capacity declines when the C₂ amine group of chitosan is modified. As described by Pearson's Hard Soft Acid Base (HSAB) theory, the C₂ amine and C₆ hydroxyl groups (classified as hard bases) form stable complexes with "borderline acid" and "hard acid" metals. Changing to the electron density in C₂ amine of chitosan alters the affinity of soft metals, for example crosslinking with glutaraldehyde turns amine into imine. Smaller electron density at the imine helps to improve adsorption for some soft acids [Cd(II)] but not borderline acids [Cu(II)]. Furthermore, conversion of primary amine to secondary amine during reductive alkylation of chitosan may also affect metal chelation due to steric effects, which may decrease the stability of metal ions chelated by C₂ amine groups. However, in some cases (when sorption occurs through ion exchange/electrostatic attraction) the steric effect of the secondary amine hardly affects sorption properties (in acidic solutions). Concurrently, the state of sulfur-containing groups of chitosan grafts affects the metal uptake where chemisorption (metal removal by formation of a strong bond such as covalent bond) is the main uptake mechanism. The potency of the thiol group to coordinate metal ions depends on the oxidation state of thiol. Oxidized thiol groups may form disulfide bonds which have a lower affinity to metal ions (Di Felice and Selloni, 2004).

The cause of poor metal adsorption capacity by modified chitosan in some instances could also be due to exhaustion of C₂ amine groups, resulting from grafting or crosslinking reactions. The number of sorption sites on chitosan may have fallen due to crosslinking that involves C₂ amine groups. The total number of metal-binding sites on a chitosan structure may be less than that of pristine chitosan if two C₂ amine groups are converted to form one sulfur-containing group. The crosslinking reaction also affects the stability of chitosan metal chelates. Pristine chitosan forms single or multiple coordination bonds between unprotonated C₂ amine and metal ions to give the "pendant" or chelate configurations (Rhazi et al., 2002). However, the chelate configurations formed by 2 or 4 coordination bonds are more stable, which, in turn, improves metal adsorption. The formation of a crosslink structure within the helical structures of chitosan disrupts the formation of metal chelates, causing weaker metal uptake. However, the impact of metal coordination configuration on metal uptake capacity is still being debated. The theoretical divalent metal uptake capacity of chitosan via a single coordination (pendant), 2 coordination or 4 coordination configuration is 6.2, 3.1, and 1.6 mmol/g, respectively (Wu et al., 2010). Even so, the lower stability of "pendant" configuration than chelate configuration may cause poor metal uptake capacity. In fact, metal uptake by pristine chitosan is likely to be within the helical structure of polymeric chitosan, chelated by 2 or 4 C₂ amine groups (Webster et al., 2007).

A comparison of metal adsorption capacities of sulfur-modified chitosan, however, is still difficult due to differences in experimental conditions as well as data interpretation. Metal adsorption parameters such as initial metal concentrations, initial adsorption pH, sorbent dosage, and temperature were different, making a fair comparison of metal uptakes of modified chitosan impossible. That is, sorption by modified chitosan at a high initial metal concentration or high pH value is likely to improve its metal uptake. Apart from this, metal sorption also increases with the porosity of modified chitosan. However, not every study used in this review reported this parameter. Consequently, high sulfur content of modified chitosan may not necessarily translate into greater metal uptake. For example, Cárdenas et al. (2001) synthesized thioglycolic acid-grafted chitosan with a sulfur content of 6.597 mmol/g and Hg(II) uptake was 0.818 mmol/g. However, the Hg(II) uptake of S2 sorbent synthesized by Gavilan et al. (2009) was 2.291 mmol/g, even with a lower sulfur content of 2.68 mmol/g. Comparing the performance of modified chitosan in removing metal is also complicated by differences in expressing metal uptake. Some reports have presented metal uptake based on removal percentages instead of metal mass uptake per unit mass of sorbent used (i.e., mmol/g). The metal removal percentage cannot describe the density of loaded metal, especially when the sorbent mass is not provided.

Another issue in sulfur modification of chitosan is the quantification of sulfur-containing functional groups in modified chitosan. An example of modified chitosan with multiple sulfur-containing functional groups is thio-carbamoyl chitosan (S1 or S2). The thioamide graft in S1 or S2 may appear as a crosslink, which enhances sorbent stability but inhibits metal uptake. Furthermore, the thermal decomposition of chitosan dithiocarbamate to thio-carbamoyl derivatives (or crosslinks) has to date not been discussed. Synthesis of dithiocarbamate with a primary amine (such as C₂ amine) is unstable at low pH or high temperature, because it decomposes into thioamide graft or a crosslink. It is therefore important to examine metal adsorption of chitosan dithiocarbamate and xanthate at broader pH ranges. Ideally, future chitosan modification should introduce large crosslinking molecules with multiple sulfur-containing functional groups (e.g., dimercapto succinic acid) to produce durable chitosan sorbent with enhanced specific surface area and metal adsorption capacity. However, these molecules are either rare or extremely expensive. Another approach would be grafting copolymers (such as polyamine oligomers) followed by introducing sulfur-containing groups to chitosan-copolymer structure, which would make sulfur enrichment more achievable.

The interactions of metal with chitosan (and derivatives) are important for designing not only metal recovery systems (for environmental purpose or metal valorization) but also for designing new materials applicable in different areas such as antimicrobial supports, catalytic systems, and sensors. Addition of sulfur to chitosan may enhance metal sorption affinity. Ironically,

if the intended end use of sulfur-modified chitosan is as cationic exchange resins, this may adversely affect its reusability. Soft acids which form coordination bonds with sulfur-containing functional groups may not be easily replaced or exchanged, thus making regeneration of spent resins difficult. However, this may be a beneficial feature as supporting material for soft acid catalysts such as Pd(II) and Pt(IV), where the loaded catalyst is reduced using in situ hydrogen from the reaction of zinc oxide and sulfuric acid (Peirano et al., 2009). Similarly, the strong interaction of soft metals with sulfur can be applied to immobilize enzymes on a biosensor. Biosensor development on chitosan was reported by Liu et al. (2004) where the gold-labeled tyrosinase enzyme was immobilized onto chitosan. The sulfur-derived chitosan membrane, or hydrogel, can immobilize enzymes by forming covalent bonds between gold-labeled enzymes with the sulfur-containing groups of chitosan (Liu et al., 2004). These are some examples of new applications of modified chitosan. Chemical introduction of sulfur-containing groups has generated new possibilities for unlocking the vast potential of chitosan.

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NOMENCLATURE

2NTAC	= 2'-aminoethylaminodeoxychitosan
6NTAC	= 6'-aminohexylaminodeoxychitosan
BH	= Chitosan with hydrogenated thiourea-glutaraldehyde graft
CHTS-MS	= Mercaptosuccinic acid-chitosan
CHTS-TH/ChEs	= Chitosan with thiirane graft
CR-azole	= Chitosan with epichlorohydrin-3-amino-1,2,4-triazole-5-thiol graft
CS ₂	= Carbon disulfide
CS-SH	= Chitosan with hydrogenated cysteamine-glutaraldehyde graft
CTS-DMTD	= Chitosan with epichlorohydrin-2,5-dimercapto-1,3,4-thiodiazole graft
CTSA	= Chitosan with salicylidene graft and chloromethyl thiirane crosslink
EDC	= <i>N</i> -(3-dimethylaminopropyl) - <i>N'</i> - ethylcarbodiimide hydrochloride

EDGE	= Ethylene glycol diglycidyl ether
EDSC	= Chitosan microsphere with 1,2-ethylenedisulfide-epichlorohydrin graft
EPI	= Epichlorohydrin
Eq. 1/TDC	= <i>N</i> -(2-hydroxyl-3-mercaptopropyl)-chitosan derivative
FTIR	= Fourier transform infrared spectroscopy
GLU	= Glutaraldehyde
H ₂ SO ₄	= Sulfuric acid
HCl	= Hydrochloric acid
HOCOCH ₂ SZ	= <i>S</i> -benzoyloxycarbonylmercaptoacetic acid
HPCM	= Highly porous chitosan microsphere
MTPC	= <i>N</i> -[3-(methylthio)propyl]chitosan
NaOH	= Sodium hydroxide
NMR	= Nuclear magnetic resonance spectroscopy
NTAC	= Aminodeoxychitosan
ONTAC	= <i>O</i> -amino-deoxychitosan
PCS/CLCT/CTS-SH	= Chitosan with chloromethyl thiirane crosslink
q_{\max}	= maximum adsorption capacity (mg/g)
QTDT	= 1,2-ethanedithiol-reduced chitosan formalidine
TCS	= Chitosan microsphere with epichlorohydrin-thiourea grafts
TMCS	= Magnetic chitosan microsphere with epichlorohydrin-thiourea grafts
TGC	= Chitosan with thiourea-glutaraldehyde graft
TMC	= <i>N</i> -(2-thienyl)chitosan
TMCR	= Thiourea modified <i>O</i> -carboxymethyl chitosan resin

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