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Journal of Chemical and Pharmaceutical Research, 2015, 7(4):49-55

Review Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Modification of chitosan for sorption of metal ions

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ABSTRACT

In recent years, environmental pollution with heavy metal ions has attracted the attention of many research groups world wide. Contamination with these heavy metal ions has also increased public concerns because of their toxicities in relatively low concentration, their non biodegradable nature and tendency of bioaccumulation. The increasing demand for the recovery of these metals from industrial effluents has stressed the development and the testing of new sorbing materials including use of abundant waste biomaterials. For last three to four decades, biopolymers have been extensively studied because of their interactions with metal ions. Cellulosics, chitin and chitosans are the most widely studied and reported biopolymers for metal ion sorption. Chitin is the main structural component of the exoskeleton of crustaceans (e.g., crabs, prawns, crabs, insects and shrimps) and the cell walls of fungi. Chitin is a polymer made up of acetylglucosamine units. In the case of some Mucorales species, chitin is replaced by chitosan, a polymer made up of glucosamine units. Chitosan is commercially produced by the deacetylation of chitin and is a typical biopolymer with excellent properties for the uptake of metal ions. Metal cations can be adsorbed by chelation on amine and hydroxyl groups of chitosan in near neutral solutions. In the case of metal anions, the sorption proceeds by electrostatic attraction on protonated amine groups in acidic solutions. However, the presence of ligands and the pH strongly control sorption performance and the uptake mechanism. Several examples are discussed with heavy metals like Cu, Zn, Ni, Cr and toxic metals like Pb, Hg and Cd. Sorption performance is also controlled by other structural parameters of the polymer (degree of deacetylation and crystallinity) that control swelling and diffusion properties of chitosan. The identification of the factors affecting sorption process helps in designing new derivatives of chitosan. Sorption properties may be improved by physical modification of chitosan including manufacturing gel beads and decreasing crystallinity. Selectivity and reusability can be enhanced by chemical modification like grafting and crosslinking. Several examples are discussed to demonstrate the versatility of the material. This versatility allows the polymer to be used under different forms ranging from water soluble form to solid form, gels, fibers and hollow fibers. These interactions of metal ions with chitosan can be used for the decontamination of effluents, for the recovery of valuable metals and also for the development of new materials or new processes involving metal-loaded chitosan. Several examples are cited in the design of new sorbing materials.

Keywords: Chitosan; metal ion; adsorption; Sorption

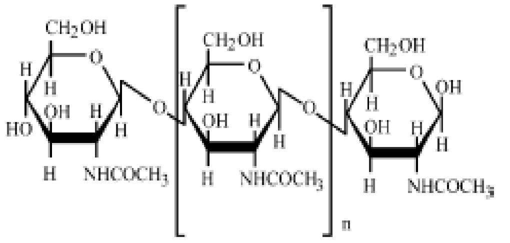
INTRODUCTION

With increasing industrialization and mining processes, environmental pollution with heavy metal ions has increased to alarming level. Heavy metal contaminants exist in air, soil and aqueous waste streams of many industries. These industries are mainly related to metal plating, leather manufacturing, mining operations, electroplating, cement ceramics, tanneries, dyeing plants and the pharmaceuticals. The soil surrounding these industries is also polluted that can further contaminate ground and surface water. Heavy metal contamination of water sources is hazardous to plants, animals and microorganism and can be carcinogenic to mankind [1,2].

The environmental contamination has increased public concerns because of their toxicities in relatively low concentration and tendency to bioaccumulation [3,4]. Heavy metals are non biodegradable and tend to accumulate in living organisms, resulting in deterioration of public health and causing various diseases and disorders [5-9]. The removal of heavy metal ions from drinking water is a real challenge due to their trace quantities, formation of complexes with natural organic matter, and toxic effect even at very low concentrations [10,11]. The improper disposal of these heavy metals can cause serious environmental problems [12].

In view of this, environmental organizations and industries are researching new methods for controlling toxic waste and minimizing or even eliminating the environmental impact [13]. Many separation methods like chemical precipitation, reverse osmosis, ion exchange and carbon adsorption have been reported to remove metal ions from wastewater [4,14]. But these methods have one or the other disadvantages. For last three decades, adsorption, ion exchange and chelation by chelating polymers especially biopolymers have widely been used for metal ion recovery because of their advantages over conventional supports. These advantages include economic and environmental advantages like their low cost, availability, reusability, easy separation, higher adsorption capacities, selectivity, ease of operation, and high removal efficiency [4,14,15,16]. Adsorption is the technique that not only can remove even trace quantities of metal ions from water but is also highly selective. Adsorption is widely used to remove heavy metals from industrial wastewaters. Detailed studies for the removal of heavy metal adsorption involving equilibrium and kinetic studies and the effects of various factors like temperature, pH and surface area have been reported [17].

Biopolymers have been extensively studied for the last 30 years because of their interactions with metal ions. These bioadsorbents in native form and chemically modified forms have been effectively used for separation of heavy metal ions from industrial waste streams. The increasing need for new and low-cost adsorbents, ever growing problems of waste disposal, the high cost of synthetic resins and high ability and selectivity of chitosan for metal sorption, make it one of the most suitable materials for wastewater treatment [18].



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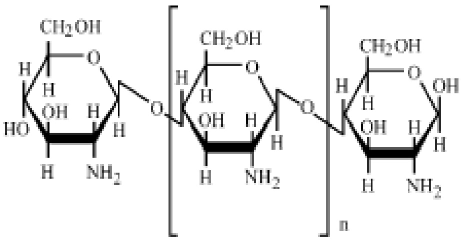
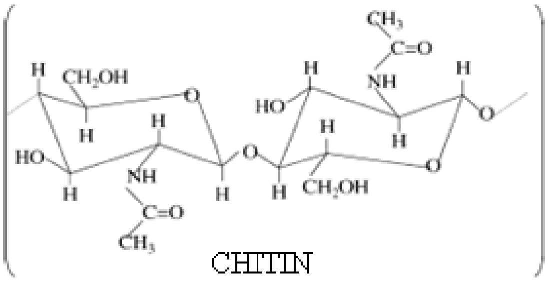


CHITOSAN

Haworth structures of Chitin and Chitosan



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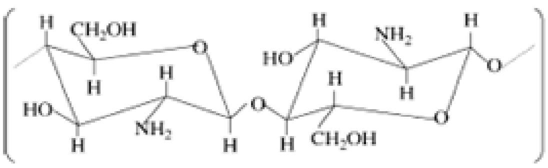

CHITOSAN

Conformational structures of Chitin and Chitosan

STRUCTURES OF CHITIN AND CHITOSAN

Chitin is the polymer of *N*-acetylglucosamine in which some of the acetyl groups (generally <50%) are lost. Chitin is an amide of acetic acid and is found as the structural polysaccharide in the exoskeleton of crustaceans such as prawns, crabs and insects and cell walls of fungi [19,20]. The major components of shells of arthropods are composed of chitin [21]. The general formula of Chitin is $(C_8H_{13}NO_5)_n$ and contains 6.9% of nitrogen. Chitosan, [Poly(1,4-ß-D-glucopyranosamine)] is partially *N*-deacetylated chitin $(C_6H_{11}NO_4)_n$ and is a primary amine. It is the second most abundant natural biopolymer. In chitosan the amino group is free and contains 8.7% of nitrogen. Unlike chitin, majority of the acetyl groups have been removed in chitosan (generally more than 70% [22]. It has same ß-(1,4)-D-glucopyranose units backbone as that of cellulose, expect for the 2-hydroxy is replaced by an acetamide group. In nut shell chitin and chitosan are high molecular weight biopolymers of glucosamine and *N*-acetylglucosamine.

MODIFICATION OF CHITOSANS FOR USE IN SORPTION OF IONIC SPECIES

Chitosans obtained from exoskeletons of different organisms have a very diverse range of applications. The great potential of chitosans is to some extent related to its poly-cationic properties. These properties are unique among polysaccharides in particular and natural polymers in general. Due to presence of both amino and hydroxyl groups, chitosan is a potential candidate for sorption of heavy metals and dyes [23]. The structure of chitosan allows excellent complexation and chelation with metal ions, particularly transition and inner-transition metals. In its native state, chitosan has some severe drawbacks those include its solubility in acidic condition ($pH < 3$) and low mechanical strength. In view of these limitations, cross linking of chitosan by suitable crosslinker is carried out that not only stabilizes it in acidic conditions but also enhances its mechanical properties [24]. It is a well established fact that chitosan may selectively complex with certain metal ions [21]. Waste water treatment that involve heavy metal and radio isotope removal with valuable metal recovery, are the main applications of metal binding property of chitosans [25].

Among many biopolymers, chitosan has the highest adsorption capacity for metals because the amino and/or hydroxy groups on chitosan chains serve as coordination sites [26]. Chitosan is a bifunctional natural polymer having amine and hydroxyl functional groups which increase its sorption capacity many times. The uptake of metal ions on chitosan may proceed through different mechanisms including chelation of metal cations on the free electronic doublet of amine groups, or ion exchange mechanisms. Nitrogen atom of amino group has one lone pair whereas oxygen atom of hydroxyl group has two lone pairs of electrons those can bind a proton or a metal ion through a lone pair of electrons forming a complex. Because of high electronegetivity of oxygen atom than nitrogen atom, the nitrogen atom has a greater tendency to donate the lone pair of electrons for sharing with a metal ion to form a metal complex than the oxygen atoms. Therefore amine groups are responsible for the uptake of metal cations by a chelation mechanism as follows [27,28]:

$$R\text{-}NH_2 + H^+ \rightarrow R\text{-}NH_3^+ \qquad (1)$$
$$R\text{-}NH_2 + M^{n+} \rightarrow R\text{-}NH_2\, M^{n+} \qquad (2)$$
$$R\text{-}NH_3^+ + M^{n+} \rightarrow R\text{-}NH_2\, M^{n+} + H+ \qquad (3)$$

Sorption properties of the polymers are also strongly controlled by the chemical modification of the polymers. Synthesis of chitosan membranes by solvent casting method has been reported [29]. These chitosan membranes complexed with different metal ions like Cu(II), Fe(III), La(III), Mo(VI) and Zr(IV) were used for As(V) sorption. Fe(III)-chitosan showed better sorption efficiency (91± 2%) for As(V) from seawater than La(III)-chitosan (80 ± 2%). These materials were further used for preconcentration of As(V) in aqueous media like tap water, ground water and seawater. Vold *et al* [30]reported methods to quantify the binding of different ions to chitosan through the determination of selectivity coefficients and also studied the influence of pH, ionic strength and fraction of acetylated units on the selectivity coefficients. ^1H NMR spectroscopy was used to determine the fraction of acetylated units. It was observed that chitosan showed no selectivity in the binding of chloride and nitrate ions, whereas high selectivity towards molybdate polyoxyanions, with selectivity coefficients around 100 was observed. Similarly, chitosan showed a strong selectivity towards copper (Cu^{2+}) compared to the metal ions zinc (Zn^{2+}), cadmium (Cd^{2+}) and nickel (Ni^{2+}), with selectivity coefficients in the range of 10 to 1000, while little or no selectivity was observed with the other metal ions. Selectivity coefficients of the chitosans towards the metal ions were not influenced by ionic strength and pH. Tabakci *et al* [31] has reported the synthesis characterization, and the evaluation of sorption properties of chitosan-linked calix[4]arene chelating polymer for sorption of heavy metal ions viz Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} Hg^{2+}, Pb^{2+} and dichromate anions $Cr_2O_7^{2-}/HCr_2O_7^-$. The sorption studies showed that chitosan-linked calix[4]arene is an excellent sorbent, while pristine chitosan was found to be poorer sorbent. The sorption studies of dichromate anions indicated that chitosan-linked calix[4]arene was highly effective sorbent at pH 1.5.

Niassar *et al* [32] has studied the effect of chitosan membrane morphology on copper ion adsorption. Macroporous chitosan membranes with various polymer concentrations and silica to chitosan ratios were synthesized. The membrane morphologies and surfaces were characterized by SEM and AFM. Adsorption experiments were performed in batch processes. It was observed that increase in the polymer concentration resulted in increased copper adsorption. Increase in the ratio of silica to chitosan resulted in greater membrane porosity and surface roughness, which made more amino groups accessible for copper ions resulting in more sorption. The amount of copper ions sorbed by the membrane with the greatest porosity and membrane roughness was found 5.9 mg/g, the highest amount achieved at an initial copper concentration of 125 ppm. Balasubramanian et al [33] reported the use of Novel beads for removal of Cr^{3+} from aqueous solutions. These beads with different ratios of poly(vinyl alcohol)/citric acid/chitosan were evaluated for the removal of Cr^{3+} ions. It was observed that the beads with poly(vinyl alcohol)/citric acid/chitosan mass ratio of 1/5/1 showed the highest adsorption for Cr^{3+} ions. The sorption kinetics data revealed pseudo-second-order equation with high regression coefficients. Langmuir adsorption isotherm has been found to describe these sorption studies to high degree of accuracy, with a maximum sorption at 41.5 mg Cr/g. The high efficiency and reusability of these beads make them an attractive sorbent for the removal of Cr^{3+} and possibly other metals in aqueous solutions.

Adsorption of Cr^{6+} on four different adsorbents i.e. activated carbon, chitosan, single-walled carbon nanotubes, and multi-walled carbon nanotubes as a function of time, pH, initial Cr^{6+}concentration, adsorbent dose, and the co presence of competing anions has been reported [34]. The extent of adsorption was found to be mximum at low pH i.e. pH 4. Out of these four adsorbents, extent of adsorption was found maximum in activated carbon and chitosan. High efficiency of activated carbon was attributed to its highly functionalized and porous nature and that of chitosan was attributed to its protonated amines. The effect of presence of organic ligands on sorption of metal ions in a solution was studied by Guibal *et al* [35]. The sorption of copper by chitosan in the presence of citrate at different metal/ligand ratios has been investigated. The results indicated that Copper uptake in acidic solution took place through electrostatic attraction between the protonated amine groups of chitosan and anionic copper-citrate complexes. Very little or no sorption took place below pH 3 due to competition from dissociated anionic ligand and counter ions brought about by dissociation of the acid used for pH control. Copper sorption was significant when the fraction of anionic copper-complexes exceeded that of anionic copper-free ligand.

A novel natural polymer chitosan/cellulose blend beads via homogeneous dissolution of chitosan and cellulose in N-Methylmorpholine-N-oxide was synthesized [36]. The SEM micrographs of these beads revealed rough and folded surface morphology and an interior pore structure. Metal ion sorption of Cu(II), Fe(III) and Ni(II) ions indicated that these beads have potential applications for metal ions adsorption. Ghaee *et al* [37] prepared macroporous chitosan membrane by particulate leaching out method for competitive adsorption of copper and nickel ions. Adsorption studies were carried out by Batch experiments with mono and binary component solutions on chitosan membrane. In mono-component, Cu^{2+} adsorption was 19.87 mg/g which was higher than those of the nickel (i.e. 5.21 mg/g), while the initial concentrations in both cases were the same. Comparing bi-component with mono-component adsorption, the competitive adsorption caused a reduction in the adsorption of individual ions. To obtain the mono and bi-component adsorption equilibrium models' parameter, several optimization methods were used and their results were compared.

The selectivity of chitosan for Cd^{2+}, Cu^{2+} and Pb^{2+} in the presence and absence of natural organic matter in different pH solutions has been reported [38]. It was found that the biosorbent selectivity at pH 4 was $Cu^{2+} > Cd^{2+} > Pb^{2+}$. Paulino *et al* [39] used chitosan-based hydrogel, graft-copolymerized with methylenebisacrylamide and poly(acrylic acid) for adsorption of Pb^{2+}, Cd^{2+}, and Cu^{2+} ions in aqueous solution. The maximum adsorption was observed at pH between 4.5 and 5.5, when initial metal concentration was 300 mg dm^{-3}. Langmuir, Freundlich and Redlich–Peterson adsorption isotherms revealed that the adsorption efficiency decreased in the presence of magnetite.

Chitosan-coated sand was utilized for removal of Cu^{2+} and Pb^{2+} ions in water. Kinetic studies revealed the pseudo second-order reaction, indicating the chemical sorption as the rate-limiting step [26]. Hydrogels of chitosan, itaconic and methacrylic acid have been used for removal of Cu^{2+} ions from aqueous solutions using batch adsorption technique. The effect of pH, adsorbent dose, initial metal ion concentration, contact time and temperature on the extent of adsorption was investigated. The FTIR spectra showed the involvement of $–NH_2$, –OH and –COOH groups in the Cu^{2+} ions adsorption. The phase images of AFM indicated that sorption took place both on the surface of the hydrogel as well as in the bulk. The equilibrium data were analyzed using Langmuir, Freundlich and Redlich–Peterson isotherms and the best interpretation was given by Redlich–Peterson. Desorption experiments indicated that these hydrogels could be reused without significant losses of the initial properties even after three adsorption–sorption cycles [40]. McKay *et al* [41] investigated the sorption of Cu^{2+} ions from solution onto chitosan at two pHs. The adsorption data were analyzed using Langmuir, Freundlich, and Redlich–Peterson equations. The Langmuir equation is the best-fit equilibrium model from three models for the sorption of copper ion onto chitosan. Ngah *et al* [42] investigated the adsorption of Cu^{2+} ions onto chitosan and cross-linked chitosan beads by using Batch adsorption experiments as a function of pH, agitation period, agitation rate and concentration of Cu^{2+} ions. Chitosan beads cross-linked with glutaraldehyde, epichlorohydrin (ECH) and ethylene glycol diglycidyl ether were insoluble in aqueous acidic and basic solution. Optimum Cu^{2+} sorption was found at a pH of 6.0. Isotherm studies indicate Cu^{2+} can be effectively removed by chitosan and cross-linked chitosan beads. Adsorption isothermal data fitted well in Langmuir equation.

Milosavljevic *et al* [43] investigated the removal of Zn^{2+} ions from aqueous solution by using novel pH-sensitive hydrogels based on chitosan, itaconic acid and methacrylic acid. The effect of pH, contact time, initial metal ion concentration and temperature on adsorption was studied. The adsorption was found to follow pseudo second order kinetics. The negative values of free energy and enthalpy indicated spontaneous and exothermic nature of adsorption. Swelling as well as adsorption capacity of the hydrogels increase with increase in temperature. Chitosan alpha-ketoglutaric acid and hydroxamated chitosan alpha-ketoglutaric acid, characterized by ^{13}C NMR and X-ray diffraction have been successfully used for the adsorption of Zn^{2+} ions. The kinetics experimental data correlated well with the second-order kinetic model, indicating chemical sorption as the rate-limiting step. N atom of amino group, O atom of hydroxamic acid and O atom of carbonyl group were found to be responsible for coordination with Zn^{2+} ions [44]. A graft copolymer of chitosan and N-vinyl formamide synthesized by free radical polymerization using bromate/cyclohexanone redox and characterized by Infra red spectroscopy and thermogravimetric analysisand swelling studies has been investigated for the sorption of Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+} and Hg^{2+} [45].

Radioactive cobalt (^{60}Co), one of the main contributors towards the activity build up in nuclear reactors, is highly toxic and its separation and isolation is essential for radioactive waste volume reduction during nuclear reactor decontamination procedures. Sorption of free and complexed Co(II), Cu(II) and nitrilotriacetic acid (NTA) on the biosorbent, chitosan was studied. Factors controlling sorption of Co(II), Cu(II) and NTA including role of pH were investigated in detail. At pH above 5, the NTA uptake was found to be higher in presence of the metal ions than in their absence. Effect of NTA was found to be more pronounced on copper uptake than on cobalt uptake. Significant change in selectivity of chitosan towards metal ion uptake from NTA medium was observed with respect to change in pH. At pH 2.9, the uptake of cobalt was found to be more than that of copper, while the selectivity was reversed at pH 6.0 [46]. Chitosan transparent thin membrane prepared by solution casting method has been investigated for adsorption of copper ions in water solution. The structure and morphology of membrane were characterized by SEM analysis and FTIR analysis. The results obtained from the study illustrated that the adsorption process could be described by the pseudo-second order model, which indicated adsorption process as a chemical adsorption [47].

Chitosan sorbents cross-linked and grafted with amido or carboxyl groups, have been used for sorption of Cu(II) and Cr(VI) uptake. Sorption studies of these metal ions at different pH values and initial ion concentrations have been carried out. The equilibrium data fitted well in Langmuir–Freundlich isotherm. Thermodynamic parameters of the sorption process were also calculated. The regeneration of sorbents was affirmed in four sequential cycles of sorption–desorption experiments, without significant loss in sorption capacity [48]. Chitosan coated on to polyvinyl chloride beads and characterized by FTIR spectra, porosity and surface area analyses has been used for adsorption of copper(II) and nickel(II) ions. Detailed studies on the factors affecting the extent of adsorption including pH, agitation time, concentration of adsorbate and amount of adsorbent was carried out. The experimental data fitted well in Langmuir and Freundlich adsorption isotherms. The experimental results indicated the chitosan coated PVC beads as effective sorbents for the removal of Cu(II) and Ni(II) ions from aqueous medium[49].

CONCLUSION

In recent time environmental pollution with heavy metal ions has increased to an alarming level. Because of their non biodegradable nature, toxicities in relatively low concentration and tendency of bioaccumulation, these metal ions are great threat not only to human health but also to all other organism. Recovery of these metals from industrial effluents has become an essential requirement of modern research and technology. This need has inspired many researchers world wide to test and develop new sorbing materials including use of abundant waste biomaterials. Technologists, researchers and scientists have extensively studied, tested and developed many sorbents derived from biopolymers. Among variety of biopolymers, chitin and chitosan, those are main structural component of the exoskeleton of crustaceans and the cell walls of fungi are the most widely studied and reported biopolymers for metal ion sorption because of their excellent interaction with metal ions. Use of these biopolymers is not only eco friendly and cost effective but their reusability is also remarkable. Sorption of metal ions takes place through chelation on amine and hydroxyl groups of chitosan. In the case of metal anions, the sorption proceeds by electrostatic attraction on protonated amine groups in acidic solutions. Sorption of ionic species on chitosan is affected both by external as well as internal environmental factors. External factors include presence of ligands, temperature and pH of solutions whereas internal factors include degree of deacetylation and crystallinity that control swelling and diffusion properties of chitosan. Chemical modification of chitosan by grafting and crosslinking not only increases efficiency of chitosan but it also increases selectivity and specificity of chitosan. Sorption properties may be improved by physical modification of chitosan including manufacturing gel beads and decreasing crystallinity. Chitosans modified by several methods have extensively been used for sorption of melals like Cu, Zn, Ni, Cr, Co Pb, Hg, As and Cd. The identification of the factors affecting sorption process helps in designing new derivatives of chitosan. From foregone discussion, it is evident that use of chitosan as biosorbent for decontamination of metal ions is a green route and it follows many of the principles of Green Chemistry.

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