A Simple Sulfuric Acid Pretreatment Method to Improve the Adsorption of Cr(VI) by Chitosan

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ABSTRACT: An optimum pH of 5.0 for the adsorption of Cr^{6+} by chitosan was determined by using a stirred-batch reactor method at constant pH. When a column containing chitosan was used to bind Cr^{6+} in a situation where pH could not be held constant because of pH changes caused by the chitosan itself, significant binding occurred only at solution pH 1 and 2. When chitosan was pretreated with sulfuric acid in a range of 7–70 mol % sulfuric acid : moles glucosamine residue, maximum binding occurred at pH 6.0. Under these conditions, a column containing 0.500 g acid-treated chitosan (35% mole ratio) reduced the concentration of Cr^{6+} in 713 bed volumes of 25 ppm Cr^{6+} solution to $\leq$5 ppm in the effluent. A similar column of pretreated chitosan reduced Cr^{6+} concentration in 1042 bed volumes of industrial chromium plating rinse water initially containing 18 ppm Cr^{6+} to $\leq$5 ppm. Capacity experiment results indicated 60 mg chromium bound per gram of treated chitosan at pH 6.0. Commercial resin IRA-67 was also investigated as a Cr^{6+} binding agent. J Appl Polym Sci 93: 2808–2814, 2004

Key words: chitosan; chromium; metal–polymer complexes; adsorption; biopolymers

INTRODUCTION

Industrial wastewater produced by chemical and manufacturing industries may contain unacceptable amounts of heavy metal ions that can cause human health problems and damage to ecosystems. Federal and often local laws mandate an upper limit to the concentration of certain metals in water discharged into public treatment plants and waterways. For example, federal regulations limit the 30-day average concentration of chromium in discharged wastewater to 2.5 ppm in electroplating wastewater and 8 ppm in leather tanning effluent.[1]

Currently, removal of metal ions from wastewater has involved using many different treatment methods including precipitation in the form of hydroxides, sulfides, or other sludges; adsorption onto a coagulated floc; electrochemical reduction; electrodialysis; and ion exchange.[2] Certain problems are associated with each of these methods: for example, precipitating sludge or floc produces toxic material that is generally impure and may require further treatment before disposal. Furthermore, precipitation methods often cannot reduce the toxic metal concentration in the wastewater to legally acceptable limits. Ion exchange and electrochemical methods require more advanced technology and are relatively expensive when compared to precipitation.

Chromium enters the waste stream as part of the process of manufacturing inks, dyes, and paints; chrome tanning of leather; and metal plating. Soluble chromium in wastewater commonly occurs in two forms: the trivalent (Cr^{3+}) and hexavalent ion (Cr^{6+}).[3] Below pH 6, hexavalent chromium is found primarily as hydrogen chromate ion, $HCrO_4^-$, and dichromate ion, $Cr_2O_7^{2-}$. Above pH 6, chromate ion, CrO_4^{2-}, becomes the dominant species.[4] Current treatment technology for removal of trivalent chromium involves precipitation as the hydroxide by using caustic soda or lime followed by dewatering and landfill disposal.[2] Hexavalent chromium is commonly first reduced to the trivalent state by using a chemical reducing agent or electrochemical reduction followed by precipitation as described above.[5] Ion exchange methods are also used to remove hexavalent chromium from wastewater.[5] In addition to being more difficult to remove from solution, hexavalent chromium is classified as a human carcinogen.[6]

Recent research has addressed the problem of metal ion removal in general, and Cr^{6+} removal in particular, through the use of biomass and biopolymers.[7,8] Of particular interest, the biopolymer chitosan was studied as an effective means of binding and removing toxic metals, including chromium, from aqueous solution.[9–11] Chitosan is a nontoxic material produced from chitin, a major component of crustacean shells.

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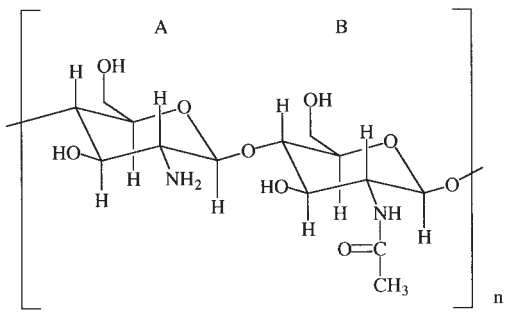

Figure 1 Chitosan. The polymer is composed of β-D-glucosamine (A) and *N*-acetyl-β-D-glucosamine (B) in an appropriate ratio of 25 : 75 with $n \sim 1000$.

Chitin and chitosan are linear copolymers of linked D-glucosamine and *N*-acetyl-D-glucosamine monomers. Commonly prepared chitin contains 70–90% *N*-acetyl-D-glucosamine with the remainder being glucosamine. Commercial chitosan typically contains 75–95% glucosamine with *N*-acetyl-D-glucosamine making up the balance (Fig. 1). Although studies have indicated that chitin is also capable of binding metal ions in solution, chitosan has shown superior metal binding performance.[9] These metal binding properties of chitosan are due in large part to its higher percentage of glucosamine residues; therefore, one of the important defining characteristics of commercial chitosan is the percentage of glucosamine present, referred to as its degree of deacetylation.[12] At 75% deacetylation, the pKa is ~ 6.5. The molecular weight of chitosan varies with processing conditions and typically ranges from 0.4 to 2×10^6 Da. An important property affected by degree of deacetylation is the solubility of chitosan in acidic solution. Chitosan containing 75% glucosamine is insoluble in water but is soluble in common inorganic and organic acids with the exception of sulfuric acid.[13] Many researchers have used crosslinking to limit the solubility of chitosan in acids, but this typically occurs at an important binding site in the glucosamine monomer, thereby reducing the binding ability of the polymer.[14]

The physical and chemical properties of chitosan vary on the basis of the chitosan source. Squid pen chitosan differs somewhat in physical appearance and properties and behaves a bit differently than crab shell chitosan, for example. Variations in the manufacturing process also will affect the degree of deacetylation, particle size, and molecular mass. Chitosan is not homogeneous in appearance, nor is it as fully characterized by its name as is a polymer such as poly(vinyl chloride).

The amine group on the glucosamine residue is considered to be the primary binding site for metal cations when the amine group is unprotonated (*R*-NH_2) and acts as a Lewis base.[15] The same site in its protonated state (*R*-NH_3^+) will then bind anions such as $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-} through an ion exchange mechanism in which these anions can be exchanged with counterions bound to the protonated amine sites. The actual mechanism and geometry of metal ion binding appear to vary from one metal species to another and are perhaps best understood in the case of copper ion binding.[15]

The ability of chitosan to bind many transition metals and main group metals without binding Group 1 or 2 elements that are often present in high concentrations in the same waste stream adds to the utility of chitosan. Furthermore, chitosan removes these transition and main group metal ions even when they are present in low concentration in aqueous solution.[9] These adsorbed metal ions can subsequently be removed from chitosan, through the use of an acid or base flush that collects the metal ions in a significantly smaller volume, more concentrated state. Because many of these toxic metals are valuable, it can be useful to have them available in a concentrated form for possible reclamation. Once the metal has been desorbed, the chitosan can be rinsed and reused.[9] When the low cost of chitosan is compared to the higher cost of ion-exchange resins, chitosan appears to offer a practical solution to many hazardous waste remediation problems.

The binding of trivalent chromium by chitosan has been well studied, but there are few published results describing binding of Cr^{6+}, a common form of chromium in industrial effluents. Previous studies on the binding of hexavalent chromium by chitosan have included, for example, an examination of binding kinetics,[16] binding capacity of chitosan,[17] and the formation of chemical derivatives of chitosan to facilitate binding of hexavalent chromium.[18] Earlier work also noted the pH dependence of binding and attempted to determine the optimum chromium solution pH that would maximize adsorption of chromium on chitosan.[16–23] Results of these pH studies show some disagreement in terms of ideal adsorption pH. Optimum pH was reported as low as pH 2 by Lopez de Alba et al.[22] and as high as pH 9 by Cha et al.[23] Most of the research identifies pH 3–4 as being most effective.[17–20] One reason for this broad reported pH binding range could be the differing properties of the various chitosans used by different researchers, or perhaps a more likely explanation is the change in solution pH caused by chitosan itself. As the mixture of chitosan in water is stirred, the pH of the water rises. This was attributed to residual sodium hydroxide from the manufacturing process or to the presence of metal ions adsorbed onto the polymer.[24] However, this pH behavior was noted by using chitosan that was dissolved in acidic solution, precipitated, and neutralized before being added to water. It was also seen in aqueous chitosan suspensions that do not contain metal ions. The pH rise could be due to the unfolding

of the chitosan chain, breaking of internal hydrogen bonds, and the protonation of the amine group by water.[25] In the majority of previous pH studies, researchers have not indicated whether the pH had been simply adjusted initially or whether it had been monitored and adjusted throughout the course of the experiment. Because of this pH rise in chitosan suspensions in water, close monitoring and adjustment of pH is necessary to establish the pH range in which metal ion binding is favored.

This work attempted to address the issues of optimum solution pH for maximum hexavalent chromium binding and to develop a pretreatment method for chitosan to enhance chromium binding capacity. Treatment methods that require the formation of a chitosan derivative bring the cost of the chitosan up to that of commercially available ion exchangers, but a simple inexpensive method could allow chitosan to be used in situations where material cost is a consideration. Muzzarelli successfully used sulfuric acid to condition chitosan prior to its use in binding some transition metal ions.[26] In the present study, a pretreatment method for chitosan using sulfuric acid was tested by using a solution of hexavalent chromium prepared in the laboratory and then applied to chromium plating rinse water obtained from a plating facility.

EXPERIMENTAL

Crab shell chitosan was purchased from CTC Organics (Atlanta, GA). The degree of deacetylation of 75%, capacity of 4.5 meq/g, and pKa of 6.3 were determined by using a titrimetric method.[27] The chitosan was either used as received from the supplier (untreated) or processed with sulfuric acid as described below (treated). The chitosan particles ranged in size from 100 to 10 mesh with no size selection performed. The weakly basic ion-exchange resin, Amberlite IRA-67 (5.6 meq/g capacity), was purchased from Sigma Chemical Co. (St. Louis, MO). All other reagents were purchased from Aldrich Chemical Co. (Milwaukee, WI) or other reputable suppliers and were used without further purification. Chromium test solutions were prepared by using potassium dichromate and ultrapure water. Rinse water from a chromium plating process contained 18 ppm Cr^{6+} as drag-out from the plating bath and was at pH 6.15 as received from a local company. The plating bath itself contained chromium trioxide, sulfuric acid, a mist suppressant, and trade secret materials. A Thermo Jerrell Ash (Waltham, MA) Unicam flame atomic absorption spectrophotometer, model 969, was used in the determination of chromium.

For experiments in which treated chitosan was used, the chitosan was stirred in concentrations of sulfuric acid that ranged from 7 to 70 mol % of the chitosan glucosamine residues for a period of 1 h. The acid was then poured off and the chitosan was air dried. The chitosan binding experiments were performed in either batch mode or in columns.

Batch tests

These tests were conducted by using 50.0 mL of an aqueous solution containing 50.0 ppm Cr^{6+}. After the pH of the solution was adjusted to the desired value in the pH range 2–10 ($\pm$0.05 pH units) using either sulfuric acid or potassium hydroxide, 0.100 g of untreated chitosan was added, and the mixture was stirred at $\geq$150 rpm for 1 h at room temperature. During this time, the pH was continuously monitored and adjusted by using either sulfuric acid or potassium hydroxide. A second test solution containing 50.0 ppm Cr^{6+} at the adjusted pH but without the addition of chitosan or stirring served as a control. After 1.0 h, the concentration of Cr^{6+} in both test solution and control was measured by using flame atomic absorption spectroscopy. Three replicates of each solution at each pH were tested.

Column tests

A 120-mm piece of 5 mm ID glass tubing was loaded with 0.500 g chitosan (untreated or treated) and packed at each end with nylon material to prevent loss or movement of chitosan. Typical bed volume was 1.2 cm^3 with a bed height of 60 mm. The pH of a 25.0 ppm solution of Cr^{6+} was adjusted to a desired integral value between 1 and 7, a pH range based on batch test results as well as early column test results. The chromium solution was pumped through the chitosan column from bottom to top at a flow rate of 0.5 mL/min and collected in postcolumn fractions of 200 drops each ($\sim$ 9 mL). This flow rate was chosen as a compromise between the relatively long contact time required for Cr^{6+} adsorption equilibrium to be established and the practical requirement of processing large volumes of wastewater.[16] The chromium content of each fraction was determined by using flame atomic absorption spectroscopy. Tests were repeated until results agreed to within 10%. Chitosan showed no evidence of swelling on contact with any of the solutions used at any pH for any length of time. After using the column method to bind chromium from the prepared test solutions, this same method involving treated and untreated chitosan was used to recover chromium from the plating rinse water. The commercial ion-exchange resin IRA-67 was tested in an identical manner, using 0.500 g of resin (1.1 cm^3 bed volume, 50 mm bed height) in the column.

Chitosan columns that had been used to remove hexavalent chromium from test solutions were regenerated by using 0.001–0.1*M* sulfuric acid and 0.1–1*M*

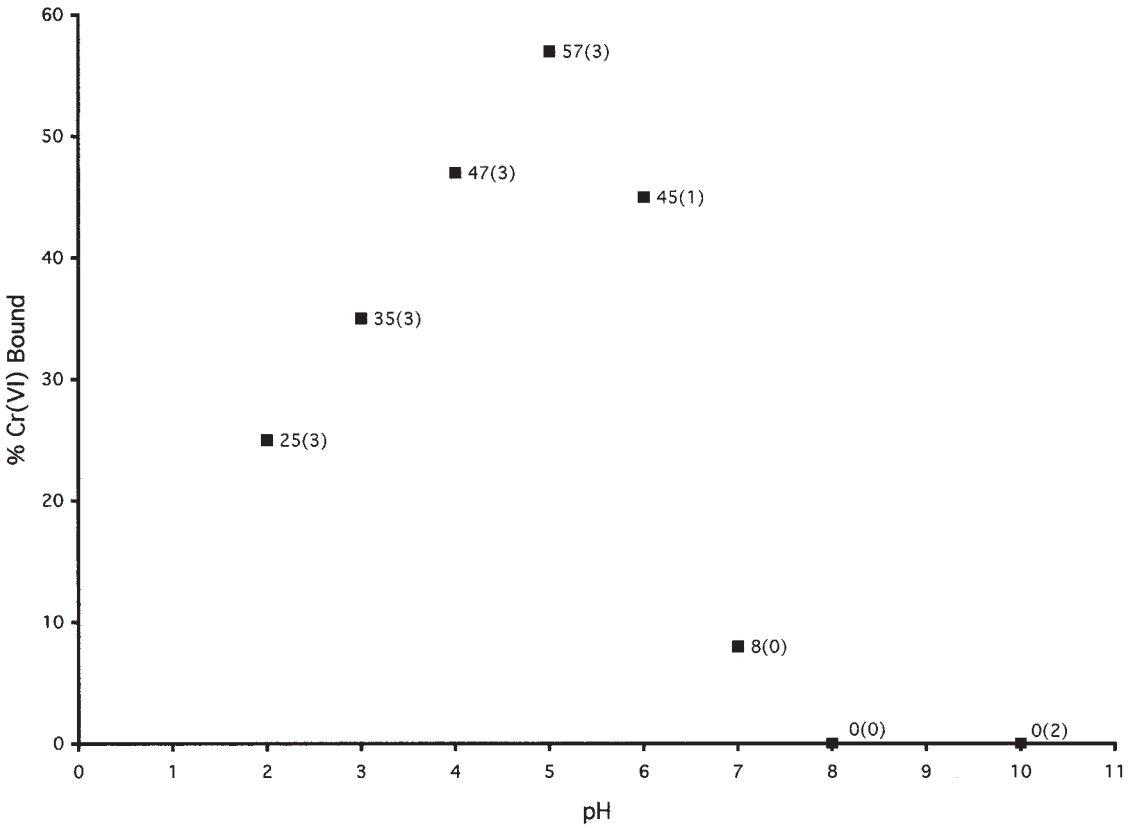

Figure 2 Percent Cr^{6+} bound by untreated chitosan using batch method at fixed pH. Number following data point lists percentage bound at that pH with standard deviation in parentheses.

potassium hydroxide to release bound chromium. These chitosan columns were then reused in subsequent binding experiments to determine the feasibility and efficacy of reuse.

A column containing treated chitosan was used to determine the binding capacity of chitosan for hexavalent chromium. A 25.0 ppm solution of Cr^{6+} at pH 6 was pumped through the column and collected as described above until the chromium concentration in the effluent rose to 95% of the concentration in the feedstock test solution.

RESULTS AND DISCUSSION

Batch tests

After the 1-h stirring period, the color of chitosan in some tests changed from off-white to yellow, indicating that chromium was indeed adsorbed by the chitosan. Results of the batch test experiments using untreated chitosan are presented in Figure 2 as percent chromium bound versus pH. These results indicate maximum binding at pH 5, a value somewhat higher than the optimal reported pH range mentioned above. This is perhaps due to the rise in pH seen in mixtures of chitosan in water. An unmonitored solution initially at pH 3 could easily rise to pH 5 during the course of a batch method experiment without pH control. If no pH measurement had been made at the end of the experiment, it would appear the adsorption occurred at pH 3, which would perhaps explain the differences in optimum pH noted in previous studies.

Column tests

Untreated chitosan column test results (Table I) are expressed as volume of 25 ppm chromium solution, given in bed volumes (BV) and milliliters, treated by the chitosan column before the concentration of chromium in the effluent reached 5 ppm. The limit of 5 ppm was chosen as representative of an acceptable concentration for disposal of industrial effluent into a public wastewater treatment facility.

Results of column tests using untreated chitosan differed from batch test results in that only under quite acidic conditions was any 25 ppm chromium solution reduced to $\leq$5 ppm by passage through the column. Untreated chitosan was able to treat only 15 BV (18 mL) of test solution at pH 1 whereas 40 BV (47 mL) was treated at pH 2. In solutions at pH 3 to pH 7, the concentration of Cr^{6+} in the effluent, although $<$25 ppm, was never reduced to 5 ppm. The chromium concentration in the first effluent fractions at pH 3–7

TABLE I
Volume of Chromium Solution Remediated by Chitosan and IRA-67 Columns as a Function of pH

	Untreated chitosan	Treated chitosan (%)					IRA-67
		7[a]	20	35	50	70	
Test solution pH							
1.0	15 (18)						
2.0	39 (47)	38 (46)	29 (35)	24 (29)	21 (25)	23 (28)	186 (205)
3.0	0	33 (40)	396 (475)	332 (398)	234 (281)	94 (113)	772 (850)
4.0	0	95 (114)	420 (504)	376 (451)	565 (678)	147 (176)	1250 (1375)
5.0	0	98 (118)	431 (517)	583 (700)	353 (424)	141 (169)	1336 (1470)
6.0	0	93 (112)	384 (461)	713 (855)	548 (658)	315 (378)	1227 (1350)
7.0	0	94 (113)	360 (432)	555 (666)	147 (176)	123 (148)	1518 (1670)
Plating rinse pH							
6.5	0	223 (268)	801 (961)	1042 (1250)	814 (977)	244 (293)	

Volumes listed represent amount of Cr^{6+} solution remediated before chromium concentration in effluent reached 5 ppm. Amounts of remediated solution are given in bed volumes followed by volume in mL in parentheses.

[a] Values in this row represent mole ratio percent (sulfuric acid : glucosamine) of the five treated chitosans.

began at ~ 10 ppm and rose in subsequent fractions collected.

In an effort to understand this lack of chromium binding in the chitosan columns, the pH of the effluent fractions from the untreated chitosan columns was measured. It was found that the pH had risen to 9–10 in the effluent when the pH of the feed solution was ≥3. At pH 9–10 no binding of chromium was expected based on batch test results. The pH rise seen in the effluent using feed solutions at pH 1 and 2 was not as dramatic. In these test solutions, the pH of the effluent more closely matched the pH of the feed solution. For example, in the case of the pH 1 feed solution, the pH of the first effluent fraction was 1.4 and remained at that value for the 10 fractions measured. When using the pH 2 feedstock in the column, the pH of the first effluent fractions was 3.0 and dropped ~ 0.1 pH unit per 9 mL fraction.

Untreated chitosan in the column mode was also used to treat chromium plating rinse water at integral, adjusted pH values of 1–5 and at the unadjusted pH of 6.15. The untreated chitosan was able to reduce the chromium concentration to ≤5ppm in 23 BV (28 mL) of the plating rinse water when the pH of the rinse water was lowered to 1 and was able to treat 67 BV (80 mL) of rinse water at pH 2. However, untreated chitosan did not reduce the chromium concentration to ≤5 ppm in any volume of rinse water at pH 3, 4, or 5 or at the unadjusted pH of 6.15.

When the rather poor results of the column tests using untreated chitosan in which the pH could not be maintained at some constant value were compared to the batch test results, the contribution of the chitosan to the pH of the system in the column tests was evident. In the batch method, with continuous pH adjustment, the pH of the system is known, and an optimal pH can be determined. However, in the column tests, the chitosan abstracts protons from the solution to protonate the amine sites, and the pH rises. Chromium binding was never very effective when using untreated chitosan in the column, quite possibly because optimum protonation of the amine sites was never achieved. Figure 2 illustrates large changes in chromium binding with small changes in pH.

Methods of treating the chitosan to improve binding were investigated because the column method seemed to be potentially more useful than the batch method in terms of technology requirements and ease of use in the removal of metal ions from wastewater. Because one of the motives for this research was the development of an effective method using easily accessible material for widespread application, lengthy or expensive processes involving the formation of chemical derivatives of chitosan appeared to be unsuitable. Ideally the treatment would be one that could be performed at low cost using readily available material by a person with minimal training. Based on the premise that chitosan with a protonated amine group would be best at binding anions such as CrO_4^{2-} and $Cr_2O_7^{2-}$, chitosan was treated with solutions of sulfuric acid. One method used here involved stirring chitosan in a batch reactor and adding sulfuric acid until a predetermined equilibrium pH was reached, for example, pH 3. Although this treatment did increase the amount of Cr^{6+} bound, the improvement was small. A second method pumped a solution of sulfuric acid in water at pH 3 through the column as a pretreatment step. The solution was pumped through the column until effluent pH was identical to feedstock pH. Approximately 600 mL of acid solution was needed to treat 0.5 g chitosan and required 20 h at a flow rate of 0.5 mL/min. Again, this treatment somewhat improved the binding of chromium by chitosan, but only 28 BV (34 mL) of test solution was treated by 0.500 g chitosan.

A third, more successful method involved mixing amounts of sulfuric acid with chitosan in varying mole sulfuric acid to mole glucosamine residue ratios that

ranged from 7 to 70%. Optimal performance in terms of enhanced binding ability was found within this range, and mole ratios > 70% were not tested. The higher mole ratios in the range were not found to be more effective, and it is assumed that not all the glucosamine residues calculated to be present were available for protonation by the acid but remained within the folded polymer. The lower volume of chromium solution successfully processed by chitosan treated with high mole ratios of sulfuric acid to glucosamine residue could be due to the high concentrations of sulfate and hydrogen sulfate anions. The presence of these anions and their involvement in ion pairing at the protonated amine site could effectively prevent the binding of chromium anions. When sodium sulfate was used to raise the sulfate ion concentration of a chromium solution at pH 5 to the sulfate ion concentration found in a chromium solution whose pH was adjusted to pH 2 using sulfuric acid, the volume of test solution remediated by the 50% mole ratio treated chitosan dropped from 353 to 104 BV. This behavior appears to agree with that seen by Muzzarelli but is in contrast to results reported by Qian et al., who saw no decrease in binding by using a 2 ppm solution of Cr^{6+} containing 3000 ppm sulfate ion at pH 3.0.[26,18]

The amount of chromium test solution that could be treated by a chitosan column rose significantly by using this sulfuric acid pretreatment. Chitosan treated with no rinsing of the polymer after the acid was poured off and air dried performed better than chitosan that was rinsed with water before being dried. Results are presented in Table I and indicate when the pH of the feed solution is low, the amount of sulfuric acid needed for pretreatment of chitosan is low. As the amount of H^+ in the solution to be remediated declines, more acid is needed in the pretreatment step to protonate the amine sites. However, consistently good results appeared when the sulfuric acid was added in a mole ratio of 35% ($\sim 1.5 \times 10^{-3}$ mol sulfuric acid/g chitosan with 75% degree of deacetylation).

The chromium plating rinse water results by using treated chitosan are also shown in Table I. Again, the best results were found by using a mole ratio of 35% sulfuric acid : glucosamine residues. The Cr^{6+} content in 1042 BV (1250 mL) of the 18 ppm rinse water was reduced to ≤5 ppm by 0.500 g chitosan.

For comparison with chitosan, the weak base ion exchange resin IRA-67 was also used to determine the amount of test solution that could be treated before the chromium concentration rose to 5 ppm. In all cases, the IRA-67 bound substantially more chromium than did chitosan (Table I). However, the high cost of the resin at ~ $30/pound is substantially more than the cost of chitosan at $8/pound.

Results of the column experiments given in Table I show less precision than the batch method experiments. This is thought to be due to some inhomogeneity in column packing and to the rather large effect of small changes in solution pH and pretreatment acid concentrations.

In column experiments where treated chitosan was used, the chitosan in the column took on a deep yellow color as chromium was bound and then a dark brown hue, perhaps indicating the reduction of hexavalent chromium to a lower oxidation state. Dambies et al. used core electron X-ray photoelectron spectroscopy (XPS) to demonstrate the reduction of Cr^{6+} to Cr^{3+} by chitosan in acidic conditions.[28] This property of chitosan adds to its suitability as a Cr^{6+} adsorbent because Cr^{3+} is not considered carcinogenic and can be handled by using other waste disposal guidelines.

After its use in removing metal ions from aqueous solution, the chitosan was recycled by using sulfuric acid or potassium hydroxide to remove the bound metal ions and reprotonate the amine group. Pumping 0.006*M* sulfuric acid through the chitosan in the column removed 80% of the bound chromium in a volume of solution that was one-sixth the original loading volume. When this regenerated chitosan was used again to bind Cr^{6+}, only 115 BV was treated before the effluent concentration reached 5 ppm, a number substantially less than the 713 BV treated by the previously unused chitosan. Bound chromium was also stripped from the chitosan by removing the chitosan from the column and stirring it with concentrations of sulfuric acid ranging from 0.0001 to 0.1*M*. The chitosan regained its off-white color, but apparently did not fully regain its binding ability for chromium. Typically, the acid-regenerated chitosan treated only 20–30% of the volume treated by virgin chitosan.

When chromium was removed by using 0.1*M* potassium hydroxide, the chitosan lost its yellow or brown color, but appeared to have a gray cast. After a neutralization and treatment step with 35% mole ratio sulfuric acid, the regenerated chitosan remained gray. Binding experiment results using this base regenerated chitosan were similar to the acid regenerated chitosan, but the base regenerated chitosan was able to treat ~ 50% of the volume treated by virgin chitosan. With further modification, the base recycling method could prove useful in practical applications.

Capacity results

The chromium ion concentration in the column effluent reached 95% of the value of the concentration in the feed solution after 2110 BV (2530 mL) of 25 ppm test solution had passed through the treated chitosan column. Based on these results, the binding capacity of treated chitosan for Cr^{6+} at pH 6.0 is 60 mg Cr/g chitosan. This number is comparable to a literature result of 78 mg/g in which chitosan and chromium were shaken together for 72 h.[17]

CONCLUSION

The work presented here indicates that a simple inexpensive pretreatment of chitosan with sulfuric acid can enhance the binding ability of chitosan for hexavalent chromium. In particular, treated chitosan performed well as an adsorbent in the case of industrial chromium plating rinse water. When the lower cost of chitosan is considered, the chromium binding properties of chitosan compare favorably to those of commercially available ion exchange resins.

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