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Effects of Acylation and Crosslinking on the Material Properties and Cadmium Ion Adsorption Capacity of Porous Chitosan Beads

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ABSTRACT

Chitosan is a novel glucosamine biopolymer derived from the shells of marine organisms. This biopolymer is very attractive for heavy metal ion separations from wastewater because it is selective for toxic transition metal ions over less toxic alkali or alkane earth metal ions. Highly porous, 3-mm chitosan beads were prepared by an aqueous phase-inversion technique for casting gel beads followed by freeze drying. In the attempt to simultaneously improve material properties and adsorption capacity, chitosan was chemically modified by 1) homogeneous acylation of amine groups with nonanoyl chloride before bead casting, and 2) heterogeneous crosslinking of linear chitosan chains with the bifunctional reagent glutaric dialdehyde (GA) after bead casting but before freeze drying. The random addition of C_8 hydrocarbon side chains to about 7% of the amine groups on uncrosslinked chitosan beads via *N*-acylation improved the saturation adsorption capacity from 169 to 216 mg Cd^{2+}/g-bead at saturation (pH 6.5, 25°C) but only slightly reduced solubility in acid solution. Crosslinking of the *N*-acylated chitosan beads with 0.125 to 2.5 wt% GA in the crosslinking bath increased the internal surface area from 40 to 224 m^2/g and rendered the beads insoluble in 1 M acetic acid (pH 2.36). However, crosslinking of the *N*-acylated chitosan beads reduced the saturation adsorption capacity to 136 mg Cd^{2+}/g-bead at 0.75 wt% GA and 86 mg Cd^{2+}/g-bead at 2.5 wt% GA. Crosslinking also significantly reduced the compression strength. There was no clear relationship between internal surface area and adsorption capacity, suggesting that the adsorbed cadmium was not uniformly loaded into the bead.

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INTRODUCTION

Biopolymers are a promising new class of adsorbents for heavy metal ion separations from aqueous process waste streams (1). Many biopolymers are inexpensive, environmentally benign, and exhibit selective binding for transition metal ions over other ionic species. Of particular interest is chitosan, a linear polysaccharide based on the glucosamine unit (Fig. 1A). Chitosan is obtained from the deacetylation of chitin, a major component of the shells of crustacean organisms and the second most abundant biopolymer in nature next to cellulose (2, 3). Interchain hydrogen bonding between hydroxyl groups on the chitin biopolymer chain make the material paracrystalline and nonporous. The amine group on each glucosamine unit within the chitosan biopolymer chain serves as a selective binding site for Group III transition metal ions, and the β-1,4-glycosidic linkage between the glucosamine units resists chemical degradation or short-term biological degradation.

The adsorption of heavy metal ions on chitosan is well documented (4–6). Rorrer et al. (7) summarized previous work on adsorption isotherm and adsorption kinetic measurements. Previous studies also attempted to define the selectivity series for adsorption of Group III transition metal ions on chitosan or chitosan derivatives (8–10). Coughlin et al. (11) demonstrated metal recovery and adsorbent regeneration by washing metal-adsorbed chitosan with acid and base solutions, respectively.

Chitosan, like most biopolymers, has two major material limitations which have hindered its development for heavy metal ion separation processes. First, chitosan is nonporous, and so must be ground to a powder to provide a sufficient surface-area-to-mass ratio for high-capacity adsorption of heavy metal ions. Furthermore, the chitosan powder is not suitable for use in packed-bed adsorption columns because of high pressure drop and the potential for bed fouling at low void fractions. Second, chitosan is readily soluble in acid solution. Therefore, the chitosan biopolymer must be engineered to a form suitable for pump-and-treat applications in aggressive chemical environments. Recently, porous beads of chitosan were synthesized for adsorption of ppm-level transition metal ions from aqueous solution (7, 10). Rorrer et al. (7) described the synthesis of large, porous-magnetic chitosan beads for cadmium ion separations from dilute aqueous solutions. Specifically, highly porous 3-mm beads were synthesized using an aqueous, phase-inversion casting technique followed by freeze drying to remove water without collapsing the porous structure of the hydrophilic chitosan biopolymer. Kawamura et al. (10) synthesized 0.6-mm chitosan gel beads with a reticular matrix, but did not use freeze

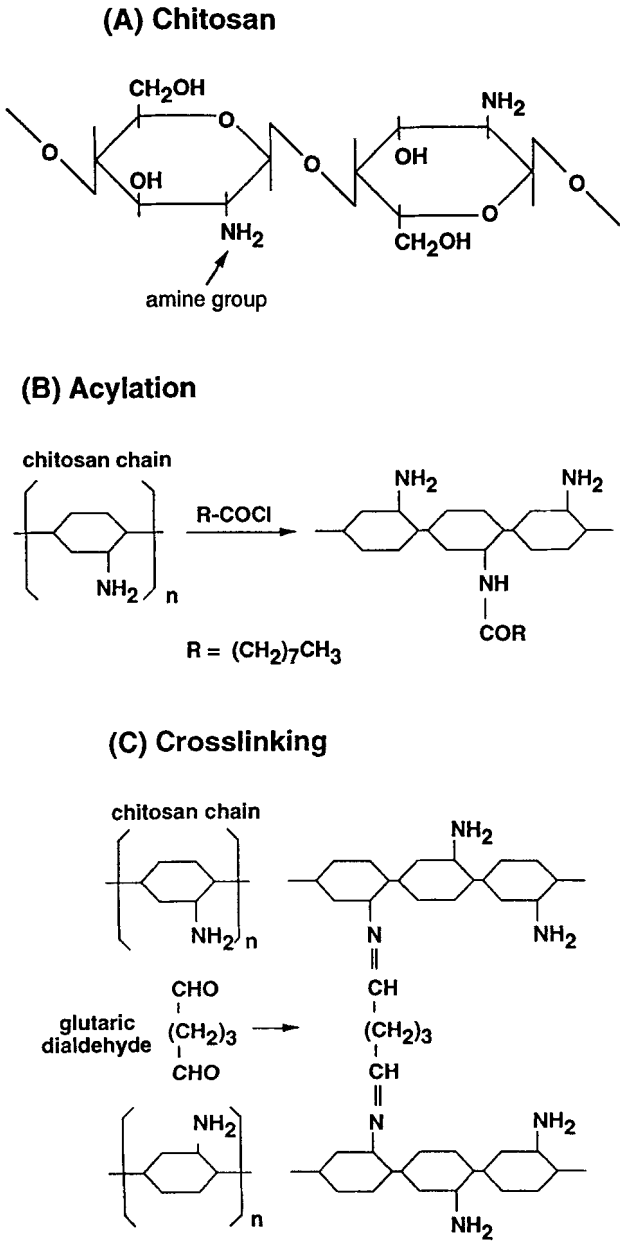

FIG. 1 Chemical structures. (A) Chitosan. (B) *N*-Acylation of chitosan. (C) Crosslinking of chitosan.

drying. Kawamura et al. showed that polyamination of the amine group significantly improved adsorption capacity for mercury ions.

The porous chitosan bead is really a biopolymer-supported reagent which can be chemically modified to alter material properties and heavy metal ion adsorption capacity. Unlike other polysaccharide biosorbents, chitosan possesses an amine group on each glucosamine residue which can serve a reactive site for two attractive chemical modifications. First, *N*-acylation of chitosan can randomly add hydrocarbon side chains to a fraction of the amine groups (Fig. 1B). These hydrocarbon site chains can impart a hydrophobic substructure to the biopolymer and also disrupt the hydrogen bonding network between chitosan chains to expose more amine sites for binding with heavy metal ions. Second, interchain crosslinking of chitosan with bifunctional reagents such as glutaric dialdehyde can impart a three-dimensional network to the biopolymer (Fig. 1B). Crosslinking can reduce the solubility of chitosan in aqueous solvents over a broad pH range, and increase resistance to chemical degradation or long-term biological degradation. Like *N*-acylation, crosslinking also can increase the spacing between chitosan chains to improve the accessibility of metal ions to amine sites. A few previous studies have described the synthesis of *N*-acylated chitosan derivatives (12, 13) and glutaric dialdehyde crosslinked chitosan (14–16). However, previous work has not considered how these chemical modifications affect material properties for porous chitosan beads.

The first objective of this study is to explore the combined effects of *N*-acylation and crosslinking on the material properties of porous chitosan beads, and their subsequent effects on the adsorption capacity for the toxic heavy metal cadmium. Specifically, chitosan will be homogeneously *N*-acylated with nonanoyl chloride at a low degree of substitution (7%) to randomly add C_8 alkyl side chains to chitosan. The *N*-acylated chitosan will then be cast into gel beads. The chitosan gel beads will then be heterogeneously crosslinked with glutaric dialdehyde and freeze dried (Fig. 2). The internal surface area, solubility in acid solution, and crushing strength will be measured to characterize the material properties of each adsorbent preparation. Adsorption isotherms for cadmium ions on each adsorbent preparation will be obtained over a broad range of Cd^{2+} concentration (5 to 1500 mg/L) in order to gain insights on how material properties affect the heavy metal ion adsorption.

Another unresolved issue in the development of chitosan biopolymer adsorbents for heavy metal ion separations is selectivity of Group III transition metal ions over Groups I and II alkali and alkaline earth metal ions. Previous studies have claimed that Groups I and II metal ions do not affect adsorption capacity transition metal ions (10, 17–19). Only Ka-

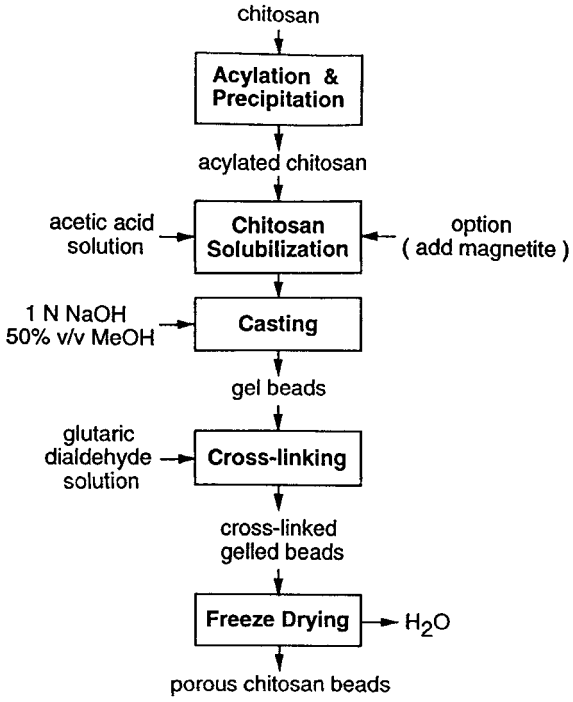

FIG. 2 Flow chart for synthesis of *N*-acylated, crosslinked chitosan beads.

wamura et al. (10) considered the effect of sodium ion concentration on adsorption capacity for mercury ions (Hg^{2+}), but the data focused on very high Hg^{2+} concentrations of 10 to 70 mM. Therefore, a second objective of this study is to measure the effect of background sodium ion concentration (0 to 150 mM) on the adsorption isotherm for cadmium ions over a broad range of Cd^{2+} concentration, specifically 5 to 1500 mg Cd^{2+}/L (0.05 to 13.4 mM).

MATERIALS AND METHODS

Chemicals

Chitosan flake (94% deacetylation) was provided by Vansen Chemical Company (Woodinville, Washington). The chitosan flake was chopped to a powder and sieved to less than 48 mesh (<300 μm). All reagents for adsorbent synthesis including acetic acid (Mallinckrodt, 2504-03), methanol (Mallinckrodt, 3041-09), pyridine (Mallinckrodt, 7180-03), glutaric di-

aldehyde (Aldrich, G400-4), and nonanoyl chloride (Aldrich, 15683-3) were ACS reagent grade. Cadmium nitrate of 98% purity was obtained from Aldrich (15683-3). The chemicals used for the preparation of eluent and postcolumn reagents for ion chromatography included oxalic acid (Aldrich, 24117-2), lithium hydroxide monohydrate (Aldrich, 25427-4), 4-(2-pyridylazo) resorcinol monosodium salt monohydrate (Dionex, PAR P/N 39672), acetic acid, and ammonium hydroxide.

Bead Synthesis

A complete flow chart for synthesis of *N*-acylated, crosslinked chitosan beads is shown in Fig. 2.

Acylation. Chitosan solution was prepared to 5 wt% concentration by dissolving chitosan powder into 0.68 M (4.2 wt%) acetic acid solution. The chitosan solution was mixed on a orbital shaker at 120 rpm for 24 hours at 25°C. After complete mixing, 70 mL of the chitosan solution was poured into 70 mL of pure pyridine and then acylated with 0.28 g of nonanoyl chloride ($CH_3(CH_2)_7COCl$), which was added to the final mixture. The mole ratio of nonanoyl chloride to amine groups on chitosan was 0.07. The acylation process was carried at 0°C for 10 minutes to avoid overreaction. The solution was then stirred at room temperature for 1 hour and finally mixed on an orbital shaker at 120 rpm for 48 hours at 27°C. After this time, the reaction was presumed complete, so that 7% of the amine groups on the chitosan chain were randomly *N*-acylated. The *N*-acylated chitosan solution was poured into pure ethyl acetate to form a gelatinous suspension of *N*-acylated chitosan. The ethyl acetate also precipitated pyridinium chloride salts formed by the acylation process. The gelatinous suspension of *N*-acylated chitosan and the pyridinium chloride salts were filtered from the ethyl acetate. *N*-Acylated chitosan was precipitated from the colloidal suspension with acetone/water (7/1 v/v). The spongy, white precipitate was washed with acetone/water (7/1 v/v) to remove the remaining salts. The *N*-acylated chitosan precipitate was stored in pure acetone to prevent oxidation.

Bead Casting. The apparatus and procedures for casting chitosan beads were described previously by Rorrer et al. (7). Chitosan solution was prepared to 5 wt% by dissolving either chitosan or *N*-acylated chitosan in 0.68 M acetic acid. The chitosan solution was delivered by a peristaltic pump at a flow rate of 0.95 mL/min to the spinnerette (0.76 mm i.d.) and dropped into a precipitation bath containing 500 mL of 2.0 M aqueous sodium hydroxide solution (NaOH). The precipitation bath was mixed at 200 rpm with a 5.5-cm marine blade impeller. Gelled beads were formed by coagulation when the acetic acid was neutralized by NaOH. Gel beads

of *N*-acylated chitosan were prepared similarly using 1.0 M aqueous methanolic sodium hydroxide solution (50% v/v) as the precipitation bath. Each bead casting run was carried out for a maximum of 4 hours. The gelled beads were filtered immediately after the casting run was complete. To impart a magnetic component to the bead, magnetite powder (60 to 100 μm) was added to the bead during the casting process as described by Rorrer et al. (7).

Crosslinking. The chitosan gel beads were heterogeneously crosslinked in aqueous glutaric dialdehyde solution (10 g wet beads in 15 mL aqueous glutaric dialdehyde solution) on an orbital shaker at 120 rpm and 25°C. The nonacylated chitosan gel beads and dry chitosan powder were crosslinked with 2.5 wt% aqueous glutaric dialdehyde solution. The *N*-acylated chitosan gel beads were crosslinked at seven glutaric dialdehyde concentrations ranging from 0.125 to 5.0 wt%, which correspond to initial —CHO/—NH_2 ratios ranging from 0.11 to 4.19 (Table 1). The crosslinking reaction was carried out for 48 hours. After crosslinking, the adsorbent was first rinsed with cold water and then with hot water to remove the unreacted glutaric dialdehyde solution.

Drying. Both acylated and nonacylated chitosan gel beads were freeze dried to slowly remove water and impart a porous structure to the beads, as described by Rorrer et al. (7). Crosslinked chitosan powder was dried in air.

Physical Properties of Beads

BET Internal Surface Area. The internal surface area of the freeze-dried chitosan beads and dry chitosan powder was determined by the BET

TABLE 1
Crosslinking Bath Parameters for Synthesis of *N*-Acylated, Crosslinked Chitosan Beads

Glutaric dialdehyde (GA) concentration in crosslinking bath (g/100 mL or wt%)	Molar ratio of bulk —CHO to —NH_2 in chitosan gel beads
0.125	0.11
0.25	0.21
0.75	0.63
1.25	1.05
2.50	2.11
3.75	3.14
5.00	4.19

method using N_2 as the adsorbate. The measurements were performed with a Micromeritics ASAP 2000 BET Surface Area and Porosimetry System. Prior to BET analysis the beads were evacuated at 70°C for 12 hours to remove gases and residual water adsorbed on the sample. The pore size distribution and mean pore size were estimated from the desorption isotherm data by the BJH method of analysis (20).

Acid Solubility. The solubility of each chitosan bead preparation in acidic solution was determined by contacting 40 mg of chitosan beads with 40 mL of 1.0 N acetic acid solution (pH 2.36) under continuous mixing on an orbital shaker at 120 rpm for 24 hours at 25°C. The percent solubility was determined from the initial and final weight of the oven-dried (85°C, 24 hours) adsorbent after 24 hour contact time.

Crushing Strength. The mechanical stability of the freeze-dried chitosan beads was estimated by a crushing strength test adapted from the ASTM Standard Test Method D-4179-82 (21). A schematic of the crushing strength apparatus is presented in Fig. 3. A single layer of 12 beads rested within the column on the base plate below the plunger. The inner diameter of the column containing the plunger was 1.23 cm. A weight resting on the top plate of the plunger applied a constant force to the sample. The end point force was determined when the irreversible displacement of the plunger was greater than 0.5 mm. The average crushing strength of beads

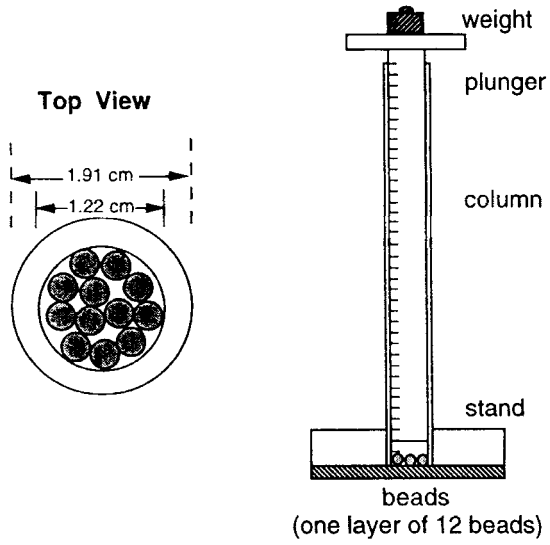

FIG. 3 Crushing strength test apparatus.

was calculated as pressure based on the end point force applied and the inner diameter of the column.

Diameter. The diameter of the chitosan beads was measured by a Vernier digital caliper. The mean diameter was estimated from a random sample of 20 to 50 beads.

Adsorption Isotherms

Adsorption Capacity. The cadmium solution was prepared by dissolving cadmium nitrate ($Cd(NO_3)_2$) in deionized distilled water. The initial cadmium ion (Cd^{2+}) concentration ranged from 5 to 2000 mg Cd^{2+}/L.

Measurements of cadmium adsorption isotherms were conducted in a well-mixed batch process which was allowed to proceed to equilibrium. The conditions for the adsorption isotherm measurement are summarized in Table 2. Specifically, 40 mg of chitosan beads were contacted with 40 mL of cadmium nitrate solution (1 g beads/L solution) within a 125-mL Erlenmeyer flask, and agitated at 120 rpm on an orbital shaker for 60 hours at 25°C. After 60 hours of adsorption, the cadmium solution was filtered from the beads. The residual cadmium solution was stored in a sealed vial for later analysis. The Cd^{2+} concentration was measured at the beginning and end of the batch adsorption experiment by ion chromatography. The final loading of cadmium adsorbed on the beads was determined by

$$Q_f = \frac{(C_0 - C_f)V}{m_b} \tag{1}$$

where C_0 is the initial concentration of Cd^{2+} (mg Cd^{2+}/L), C_f is the final concentration of Cd^{2+} at equilibration (mg Cd^{2+}/L), m_b is the mass of

TABLE 2
Summary of Conditions for Adsorption Isotherm Measurement

Process condition	Variable and units
Contact time	60 hours
Temperature	25°C
pH	6.5–7.0
Bead loading	1 g/L
Solution volume	40 mL in 125 mL flask
Agitation	120 rpm (orbital shaker)
Initial cadmium concentration	5 to 1500 mg Cd^{2+}/L

beads, Q_f is the adsorption capacity of Cd^{2+} on the bead (mg Cd^{2+}/g-adsorbent), and V is the volume of solution (L).

Ion Chromatography. The Cd^{2+} concentration in each sample was determined by ion chromatography (IC) using a Dionex model DX-300 Ion Chromatograph. The IC hardware system consisted of an automatic sample injector with 100 μL sample loop, dual-piston gradient high pressure pump, PAR postcolumn reaction coil, and a UV/VIS variable wavelength detector. All wetted parts were constructed of nonmetallic materials, including polyether ether ketone (PEEK). A Dionex CG-5 guard column and CS-5 transition metal analysis column (4 mm i.d., 25.4 cm packing length) were used to profile the transition metal ions in the sample. The UV/VIS detector was connected to an AST-286 PC equipped with Peaksimple II interface board and software (SRI Instruments).

Prior to analysis, 0.5 mL of sample was added to 0.5 mL of 20.5 mg/L cobalt (Co^{2+}) in 1 wt% HNO_3. The Co^{2+} served as an internal standard. A 100-μL aliquot of the solution (Cd^{2+} plus Co^{2+} as the internal standard) was injected into the IC system and separated by the CS-5 column at 25°C using 0.07 M oxalic acid as the eluent at a constant flowrate of 1.00 mL/min. The eluent was adjusted to pH 4.8 with lithium hydroxide monohydrate (0.095 M). The separated metal ions were chelated with 4-(2-pyridylazo) resorcinol monosodium salt monohydrate (PAR) to form a chromophore in the PAR postcolumn reaction coil, and then profiled by the UV/VIS detector at an absorbance of 520 nm. The retention times for Cd^{2+} and Co^{2+} (the internal standard) were 5.8 and 7.3 min, respectively. The metal ion peaks were integrated, and the concentration of Cd^{2+} was determined by the internal standard method.

RESULTS AND DISCUSSION

Physical Properties of Porous Chitosan Beads

The physical properties of the chitosan adsorbents, including diameter, BET surface area, solubility, and crushing strength are summarized in Table 3.

As shown in Table 3, the combination of *N*-acylation and crosslinking resulted in the highest internal surface area for the chitosan beads. The average internal surface area of the *N*-acylated chitosan gel beads crosslinked with 2.5 wt% glutaric dialdehyde was 223.6 m^2/g after freeze drying versus 192.4 m^2/g for nonacylated chitosan beads crosslinked and freeze dried under the same conditions. The average internal surface area of uncrosslinked *N*-acylated chitosan beads was only 42.6 m^2/g, showing clearly that crosslinking was required to impart a high internal surface area to the beads. However, heterogeneous crosslinking of the chitosan

TABLE 3
Summary of Physical Properties for Selected Chitosan Adsorbent Preparations

Chitosan adsorbent	Mean particle diameter (mm)	Magnetite content (wt%)	N_2-BET surface area[a] (m^2/g)	Acid solubility (wt%)	Differential crushing strength (psi)
Uncrosslinked chitosan powder	<0.3	0.0	15.9	99.3	N/A
Crosslinked chitosan powder	<0.3	0.0	1.9	12.4	N/A
Uncrosslinked chitosan beads	3.3 ± 0.3	13.2	60.1 ± 7.7 (n = 2)	99.0	16.4
Crosslinked chitosan beads	3.2 ± 0.1	12.2	192.4 ± 20.7 (n = 3)	4.6	4.8
N-Acylated chitosan beads	3.3 ± 0.2	13.8	42.6 ± 12.9 (n = 4)	96.5	16.4
N-acylated, crosslinked chitosan beads	3.2 ± 0.1	13.8	223.6 ± 10.6 (n = 3)	0.3	2.3

[a] Average values and standard deviations reported for n repeat batch preparations.

powder reduced the internal surface area from 15.9 m^2/g to only 1.9 m^2/g, indicating that only heterogeneous crosslinking of the chitosan gel bead followed by freeze drying improved the final internal surface area. Therefore, *N*-acylation, bead casting, crosslinking, and freeze drying steps must be combined to maximize the internal surface area of the chitosan adsorbent.

The material properties of the *N*-acylated chitosan beads were significantly affected by crosslinking with glutaric dialdehyde. The concentration of glutaric dialdehyde in the crosslinking bath was the most critical variable for the crosslinking process. Figure 4 shows the effect of the glutaric dialdehyde concentration in the crosslinking bath on the internal surface area and acid solubility of the 3-mm *N*-acylated chitosan beads. The internal surface area of the crosslinked *N*-acylated chitosan beads increased as the concentration of glutaric dialdehyde in the crosslinking bath increased from 0.125 to 2.5 wt%. However, the internal surface area decreased slightly when the glutaric dialdehyde concentration was increased to 5.0 wt%.

Crosslinking also significantly reduced the solubility of chitosan in dilute acid. Chitosan adsorbents that were not crosslinked were readily soluble. The solubility of chitosan adsorbents was determined by measuring the percentage of chitosan that did not dissolve in 1 M acetic acid solution

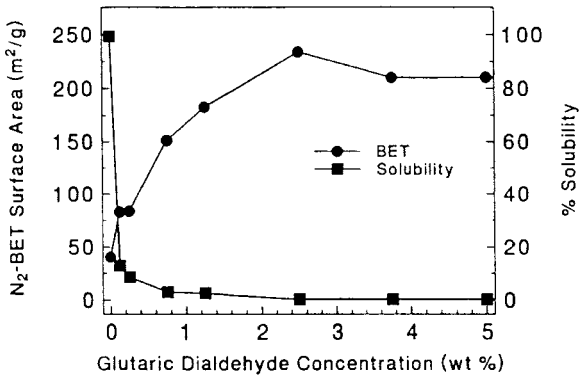

FIG. 4 Effect of glutaric dialdehyde concentration in the crosslinking bath on internal surface area and acid solubility for *N*-acylated chitosan beads.

(pH 2.36) after 24 hours at room temperature. On average, 96.5% of the chitosan in the uncrosslinked *N*-acylated chitosan beads dissolved in the acetic acid solution after 24 hours. The solubility of the crosslinked *N*-acylated chitosan beads decreased drastically from 96.5 to 0.3% as the glutaric dialdehyde concentration in the crosslinking bath was increased to 2.5 wt% (Fig. 5). The type of the chitosan adsorbent used for crosslinking also affected the acid solubility. *N*-Acylated, crosslinked chitosan

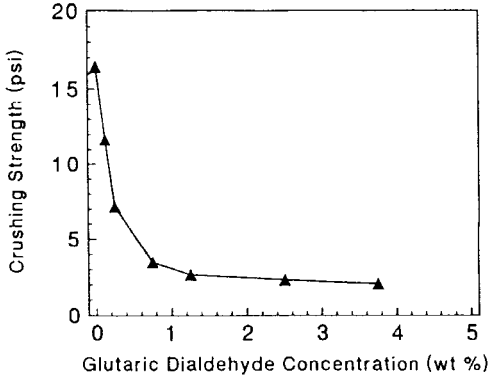

FIG. 5 Effect of glutaric dialdehyde concentration in the crosslinking bath on the crushing strength of *N*-acylated chitosan beads.

beads had the lowest solubility of 0.3 wt%, compared to 4.6 wt% for the nonacylated crosslinked chitosan beads and 12.4 wt% for the crosslinked chitosan powder (Table 3). Apparently, the hydrocarbon chains on *N*-acylated, crosslinked chitosan beads increased the hydrophobicity of the biopolymer and hence helped to reduce the acid solubility. However, *N*-acylation alone was not successful in reducing acid solubility (Table 3).

The effect of glutaric dialdehyde concentration in the crosslinking bath on the crushing strength of *N*-acylated chitosan beads is presented in Fig. 5. Crushing strength measurements were performed only on the final freeze-dried chitosan beads, not the chitosan gel beads before freeze drying. The uncrosslinked *N*-acylated chitosan bead had the highest crushing strength, 16.4 psi. The differential crushing strength of *N*-acylated chitosan beads decreased as the glutaric dialdehyde concentration in the crosslinking bath increased from 0.125 to 2.5 wt%, and then leveled off at 3.75 wt%. The differential crushing strength of the *N*-acylated chitosan bead crosslinked in 3.75 wt% glutaric dialdehyde solution was 2.0 psi, 8 times smaller than the uncrosslinked *N*-acylated chitosan beads. *N*-Acylation of the chitosan bead without crosslinking did not have a significant effect on crushing strength (Table 3).

Crosslinking may have reduced the crushing strength of the beads by shifting the void fraction from macropores to mesopores as the internal surface area increased. Crosslinking may have also rendered the biopolymer itself less elastic to compression forces. In particular, the rigid double bond between the dialdehyde groups and amine groups for the crosslinked chitosan may have reduced the elasticity of the linear chitosan chain and disrupted the hydrogen bonding network between the chitosan chains, making the material more brittle.

In summary, crosslinking of chitosan beads between the dialdehyde group (—CHO) on glutaric dialdehyde and amine group ($—NH_2$) on chitosan increased the internal surface area, reduced the acid solubility, and reduced the crushing strength. However, the internal surface area, acid solubility, and crushing strength of beads leveled off at high concentrations (2.5 wt%) of glutaric dialdehyde in the crosslinking bath. Apparently, at high glutaric dialdehyde concentrations, a significant fraction of the amine groups near the outer surface of the bead were crosslinked. This highly crosslinked outer shell most likely determined the final material properties of the chitosan bead. The consumption of glutaric dialdehyde in the crosslinking bath was not measured, and so the true extent of crosslinking in this outer shell is not known. Conditions of bead casting, *N*-acylation, and crosslinking must ultimately be optimized to synthesized chitosan beads of desired internal surface area, stability in acid solution, and crushing strength.

Cadmium Ion Adsorption Isotherms

Adsorption isotherms for cadmium ions on chitosan beads and chitosan powder were obtained at pH 6.5 and 25°C. The effects of background sodium ion concentration, crosslinking, and *N*-acylation on the adsorption isotherms were considered.

The cadmium adsorption isotherms for nonacylated, crosslinked chitosan beads in background concentrations of $NaNO_3$ ranging from 0 to 150 mM are shown in Fig. 6. The cadmium uptake of nonacylated, crosslinked chitosan beads was not affected by the presence of sodium ions at 50 and 150 mM over the cadmium ion concentrations ranging from 5 to 1500 mg/L. The effect of alkali and alkaline earth metal ions on transition metal adsorption capacity has not been investigated thoroughly, especially for Cd^{2+} binding on chitosan. Jha et al. (22) showed that the presence of 5 mM Ca^{2+} decreased the Cd^{2+} adsorption rate on chitosan powder during the first 24 hours of adsorption. After 24 hours the adsorption capacity decreased only 7% at cadmium ion concentrations ranging from 1 to 10 mg/L. Muzzarelli and Tubertini (17) showed that the presence of sodium ions in seawater did not affect the adsorption capacity of transition metal ions on chitosan, but data were obtained at only one transition metal ion concentration of 0.044 mM.

The results show that sodium cations do not hinder the chelation of Cd^{2+} ions with the amine groups on chitosan. The electron orbital configuration of Na^{+}, a Group IA alkali metal, has only s and p electrons in its

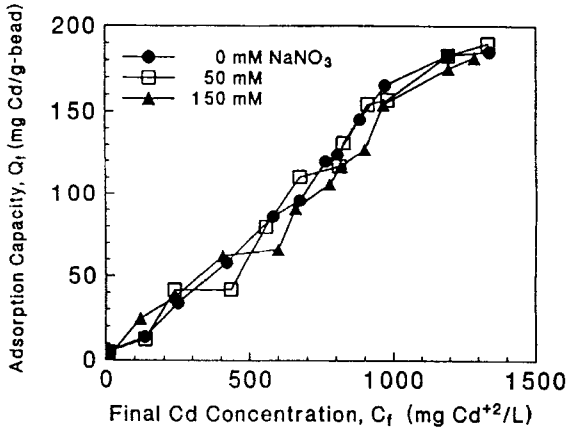

FIG. 6 Effect of background $NaNO_3$ concentration on the cadmium adsorption isotherm for nonacylated, crosslinked chitosan beads.

outer shell. In contrast, Cd^{2+} possesses s, p, and unsaturated d electron orbitals in its outer shell. Thus, Cd^{2+} selectively binds to chitosan by the chelation of unfilled d electron orbitals on the Cd^{2+} ion with the p orbital on the amine group, similar to the Co^{2+} binding on ammonia ligands (23).

The effect of crosslinking on the cadmium adsorption isotherms for the nonacylated chitosan beads is shown in Fig. 7. Both of the isotherms have a similar stepped shape. The behavior of the stepped shape of the adsorption isotherm was discussed earlier by Rorrer et al. (7). The uncrosslinked chitosan beads have a slightly higher adsorption capacity than the crosslinked chitosan beads at final cadmium ion concentrations ranging from 100 to 500 mg/L. The adsorption capacity did not change significantly between the uncrosslinked and crosslinked nonacylated chitosan beads at final cadmium concentrations ranging from 600 to 1500 mg/L. These results are surprising since the internal surface area of the uncrosslinked chitosan beads (60.1 m^2/g) was significantly lower than the crosslinked chitosan beads (192.4 m^2/g). Apparently, the cadmium was not loaded uniformly in the bead. Therefore, other material properties, such as the pore size distribution or the structure of crosslinked outer shell, may have also affected the adsorption capacity. In particular, the highly-crosslinked outer shell could have hindered diffusion of Cd^{2+} ions into the center of the bead. A diffusion mechanism which further suggests that the metal would be preferentially loaded near the outer surface of the porous bead is described by Rorrer et al. (7).

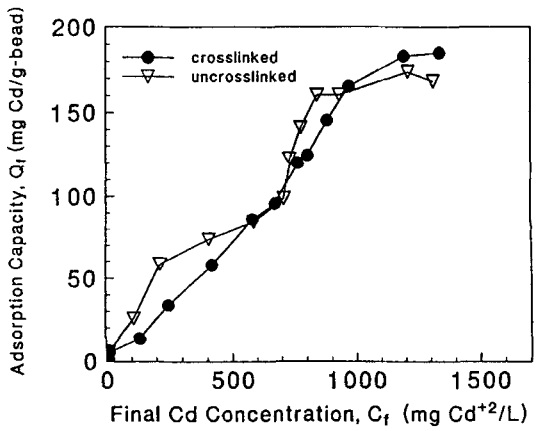

FIG. 7 Effect of crosslinking on the cadmium ion adsorption isotherm for nonacylated chitosan beads.

The effect of crosslinking on the cadmium adsorption isotherms for the finely-ground nonacylated chitosan powder is presented in Fig. 8. Although the chitosan powder was sieved below 300 μm, a significant fraction of the particles were around 100 μm. At saturation, the uncrosslinked chitosan powder had twice the cadmium adsorption capacity of the crosslinked chitosan powder. Yang and Zall (5) proposed that the overall adsorption rate of metal ions was controlled by the diffusion rate into the chitosan powder. Apparently, the majority of the adsorbed cadmium was concentrated near the surface of the chitosan powder. The reduction in adsorption capacity for the nonacylated crosslinked chitosan powder probably resulted from the reduction of exposed amine sites near the surface as the result of the heterogeneous crosslinking process. To support this conclusion, the BET surface area of the uncrosslinked chitosan powder was 15.9 m^2/g versus only 1.91 m^2/g for the crosslinked chitosan powder.

Masri et al. (14) suggested that the adsorption capacity of transition metal ions on chitosan powder was reduced by a heterogeneous crosslinking process with glutaric dialdehyde. In contrast, Koyama and Taniguchi (15) homogeneously crosslinked chitosan with glutaric dialdehyde in acetic acid solution and claimed that the adsorption capacity for Cu^{2+} increased as a result of the crosslinking process. Specifically, they proposed that the homogeneous crosslinking chitosan at an initial —CHO/—NH_2 ratio of 0.7 increased the hydrophilicity of chitosan and improved the

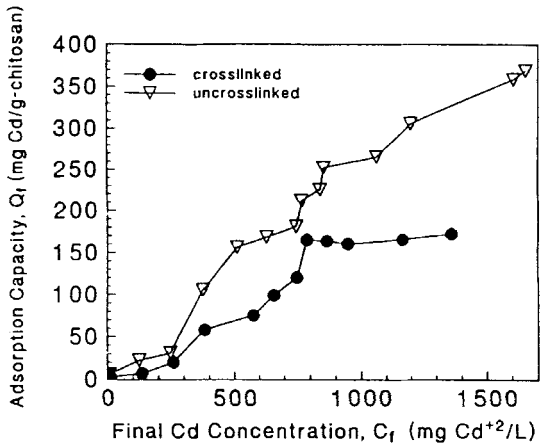

FIG. 8 Effect of crosslinking on the cadmium ion adsorption isotherm for nonacylated chitosan powder.

accessibility of metal ions to amine groups by disruption of the crystalline structure. In this study, when the chitosan beads were synthesized, both the porosity of the bead and the crosslinking reaction affected the number of readily accessible amine sites. The amine groups consumed by crosslinking were presumably compensated for by an increase in the number of amine sites exposed by the increased internal surface area. However, the true number of exposed amine sites within the porous matrix could not be measured directly. Direct titration of the exposed basic amine sites with acid was not possible as the hydrogen ions would penetrate into the nonporous regions of the chitosan bead and swell the biopolymer.

The effect of crosslinking on the cadmium adsorption isotherms for the *N*-acylated chitosan beads is shown in Fig. 9. There was no significant difference in adsorption capacity between the *N*-acylated chitosan beads at final cadmium ion concentrations ranging from 4 to 200 mg/L. However, the difference in adsorption capacity became significant when the final Cd^{2+} ion concentration was above 700 mg/L. In particular, the slope of the adsorption isotherm decreased drastically when the *N*-acylated chitosan bead was crosslinked at higher glutaric dialdehyde concentrations. This reduction in adsorption capacity may have resulted from the combined stearic hindrance of amine, alkyl, and aldehyde functional groups to the binding of cadmium ions to exposed amine sites within the chitosan bead.

N-Acylation without crosslinking improved adsorption capacity for Cd^{2+} on the chitosan beads at concentrations exceeding 1000 mg Cd^{2+}/

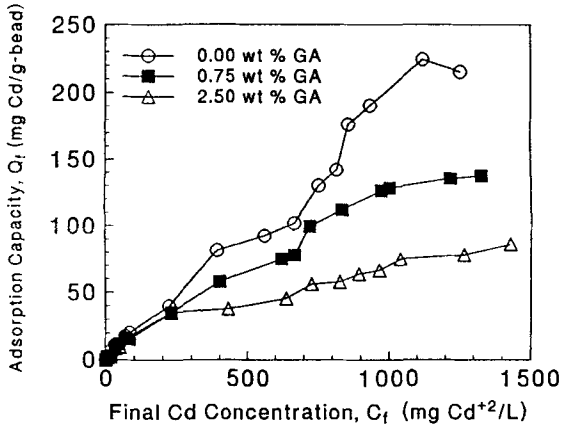

FIG. 9 Effect of glutaric dialdehyde concentration in the crosslinking bath on the cadmium ion adsorption isotherm for *N*-acylated chitosan beads.

L. The saturation adsorption capacity was 216 mg Cd^{2+}/L for the *N*-acylated, uncrosslinked chitosan beads, versus 169 mg Cd^{2+}/L for nonacylated, uncrosslinked chitosan beads, an increase of about 28%.

Low Cd^{2+} concentration adsorption isotherms over the range of 4 to 80 mg Cd^{2+}/L are presented in Fig. 10. The nonacylated, uncrosslinked chitosan beads had the highest adsorption capacity. The adsorption capacity of the *N*-acylated, crosslinked chitosan beads were comparable with one another. The binding of Cd^{2+} on the *N*-acylated, crosslinked chitosan beads exhibited type V isotherm behavior, suggesting weaker adsorbate/adsorbent interactions in mesoporous solids (24). At low Cd^{2+} concentrations, the driving force for diffusion of Cd^{2+} ions into the porous bead was low. Thus, the binding of Cd^{2+} to the chitosan may have been localized near the outer surface of bead. The nonacylated, uncrosslinked chitosan beads had the highest number of potential external adsorption sites near the surface. In contrast, the number of exposed amine sites on the *N*-acylated, crosslinked chitosan bead were decreased by *N*-acylation and crosslinking reactions.

Isotherm data over the low concentration range of 4 to 80 mg Cd^{2+}/L were fitted to the Freundlich isotherm, given by

$$Q_e = KC_e^{1/n} \tag{2}$$

where K and n are adjustable parameters. The parameter K is a measure of the adsorption capacity or binding strength, whereas $1/n$ is a measure of adsorption intensity. The value for n is also an indicator of the distribution of bond strengths. When $n > 1$, then the bonding energy decreases with increasing surface concentration. Log-log plots of Q_e vs C_e data have

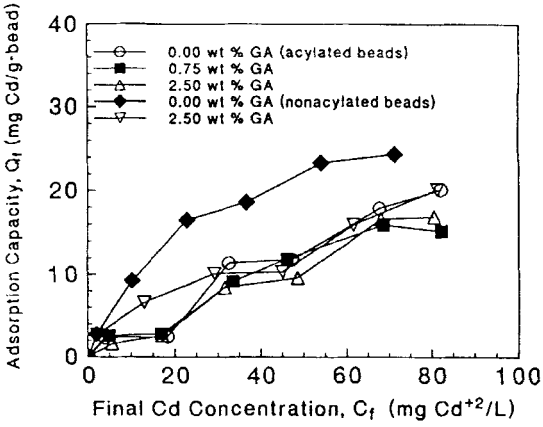

FIG. 10 Low concentration adsorption isotherms (4–80 mg Cd^{2+}/L).

TABLE 4
Freundlich Parameters for Low-Concentration Cd^{2+} Isotherm Data

Adsorbent preparation	K	n	r^2
Uncrosslinked chitosan beads	2.01	1.61	0.98
Crosslinked chitosan beads (2.5 wt% GA in crosslinking bath)	1.76	1.97	0.97
N-Acylated, uncrosslinked chitosan beads	0.59	1.30	0.81
N-Acylated, crosslinked chitosan beads (0.75 wt% GA in crosslinking bath)	0.61	1.35	0.87
N-Acylated, crosslinked chitosan beads (2.5 wt% GA in crosslinking bath)	0.26	1.06	0.95

slope $1/n$ and intercept log K. Values for K and n are given in Table 4. The data fitted the Freundlich isotherm model reasonably well with 3 of the 5 isotherms having an r^2 value of 0.95 or above. *N*-Acylation of chitosan reduced the values for both K and n. This analysis suggests that *N*-acylation decreases the adsorption capacity and binding strength while promoting monolayer coverage of the adsorbed metal on the exposed surfaces of the adsorbent at low Cd^{2+} concentrations.

SUMMARY AND CONCLUSIONS

Glucosamine biopolymers such as chitosan are a promising new class of adsorbents for heavy metal ion separations. However, the chitosan biopolymer must be engineered into a form which exhibits high adsorption capacity and stability in low-pH chemical environments. To address these needs, 3 mm porous chitosan beads were fabricated using an aqueous phase inversion technique to cast gel beads followed by freeze drying of the gel beads to remove water without collapsing the pore structure. In the attempt to simultaneously improve material properties and cadmium ion adsorption capacity, two chemical modifications to the chitosan beads were considered. First, before bead casting, C_8 alkyl side chains were added to chitosan at a 7% degree of substitution by homogeneous *N*-acylation with nonanoyl chloride. Second, the chitosan gel bead was heterogeneously reacted with the bifunctional reagent glutaric dialdehyde to form a highly crosslinked outer shell. Both acylation and crosslinking attempted to impart hydrophobicity to the biopolymer and increase the spacing between biopolymer chains in order to reduce solubility and improve access of transition metal ions to amine adsorption sites.

The combination of acylation, bead casting, crosslinking, and freeze-drying steps produced a highly porous chitosan bead which was insoluble

in 1 M acetic acid solution (pH 2.4) and possessed an internal surface area of 224 m^2/g. The concentration of glutaric dialdehyde in the crosslinking bath was the most important process variable for determining the material properties.

N-Acylation and crosslinking also effected the adsorption capacity for cadmium ions. *N*-Acylation of uncrosslinked chitosan beads improved the saturation adsorption capacity from 169 to 216 mg Cd^{2+}/g-bead. However, crosslinking of the *N*-acylated chitosan beads reduced the saturation adsorption capacity down to 136 and 86 mg Cd^{2+}/L when the glutaric dialdehyde concentration in the crosslinking bath was increased to 0.75 and 2.5 wt%, respectively. In contrast, at low concentrations of 4 to 80 mg Cd^{2+}/L, the adsorption capacities were comparable. Analysis of the Freundlich isotherm parameters for nonacylated and *N*-acylated chitosan beads inferred that *N*-acylation decreased the adsorption capacity and binding strength for Cd^{2+} while promoting monolayer coverage of the adsorbed metal on exposed surfaces of the adsorbent. All trends suggested that the cadmium metal was preferentially loaded near the outer surface of bead, as there was no clear relationship between internal surface area and the adsorption capacity.

This paper has shown that chitosan is a facile biopolymer-supported reagent for chemical modifications leading to improved material properties. However, the relationship between the material properties and the cadmium ion adsorption capacity is complex. Future studies will attempt to more clearly define this relationship by relating chemical microstructure of the bead to the distribution of adsorbed metal within the bead.

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