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Adsorption of Metal Ions on Gallium(III)-Templated Oxine Type of Chemically Modified Chitosan

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ABSTRACT

The oxine type of chemically modified chitosan was prepared by the template crosslinking method employing gallium(III) ion as a template ion. The functional groups of oxine were found to be incorporated into the polymer chain of chitosan at a oxine/glucosamine unit ratio of 1/3. This value agrees with that expected from molecular modeling computation by the molecular mechanics method. Adsorption of molybdenum(VI), vanadium(IV), indium(III), aluminum(III), zinc(II), iron(II), and cadmium(II) together with gallium(III) on this chemically modified chitosan from dilute sulfuric acid solution was compared with that on the original chitosan. It was found that the pH at which the adsorption of these metals takes place on this chemically modified chitosan shifted to a lower pH than that on the original chitosan. The shift was the greatest for gallium(III) among the metal ions examined, which might be attributable to the template effect of gallium(III) ion. The maximum adsorption capacity of gallium(III) was evaluated as 1.17 mol/kg-dry adsorbent. The selective adsorption of small amounts of gallium(III) and indium(III) from an excess amount of zinc(II) was confirmed from the breakthrough profile of separation using a column packed with this chemically modified chitosan.

Key Words. Adsorption; Metal ions; Chemically modified chitosan; Template crosslinking method; Molecular modeling computation

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INTRODUCTION

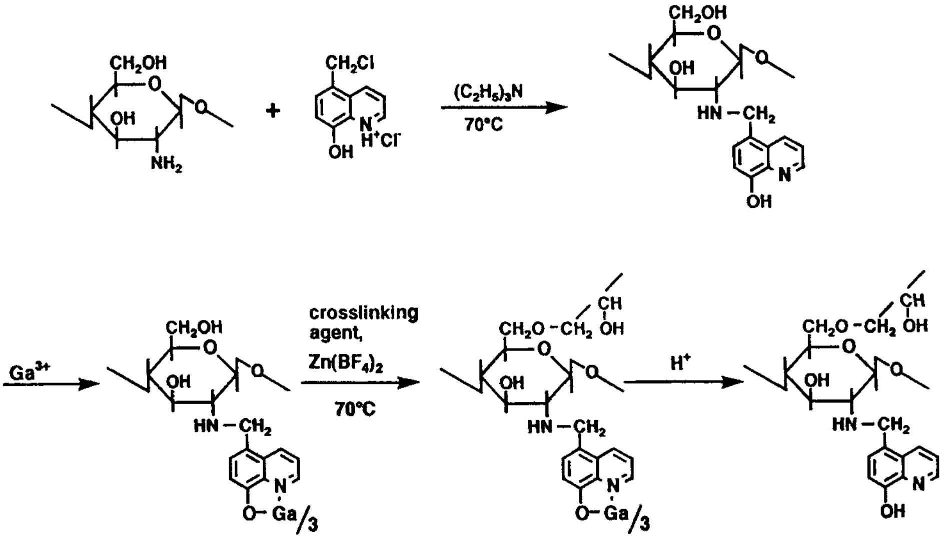
Owing to the high stability of its complexes with various kinds of metal ions, chelating resins incorporating functional groups of oxine have been known for more than 50 years since Erlenmeyer and Dahn first attempted the separation of cations on columns of powdered oxine (1). This type of resin became commercially available under the trade name Spheron Oxine 1000 (Koch-Light laboratories) (2, 3). Most of the methods of synthesis described in the literature are modifications of the original three methods: condensation of oxine, resorcinol, and formaldehyde (4, 5); coupling a diazotized polyaminostyrene resin with oxine (6); and bonding a polystyrene resin with chloromethyloxine or a chloromethylated polystyrene resin with oxine by a Friedel–Crafts acylation (7). However, these methods provide resins with low capacities and slow rates of exchange, and the metal adsorption properties of the resins have been far from satisfactory. This is considered to be partly due to insufficient swelling of the resin during preparation and partly to steric hindrance of polymer chains which makes it difficult to prepare the resin with functional groups incorporated at suitable positions on polymer matrices to give rise to metal-chelates fully satisfying both of the requirements of coordination and electrical neutrality of the adsorbed metal ions. It was reported that Spheron Oxine 1000 resin gives rise to copper(II)-chelates with compositions of both 1:2 metal:oxine and also 1:1 unsatisfied chelate (3). Contrary to synthetic polymers such as crosslinked polystyrene, chitosan, a natural polymer, is free from the problem of swelling owing to its high hydrophilicity with a large number of hydroxyl groups. In addition, owing to the flexible structure of its polymer chains, it may not be difficult to prepare chitosan-based metal adsorbents with high selectivity and high loading capacity by means of simple chemical modification by incorporating large number of functional groups at suitable positions on its polymer matrices which would enable a suitable configuration for the formation of stable chelates because of the large number of highly reactive primary amino and hydroxyl groups.

In the present work we prepared a novel type of chemically modified chitosan incorporating functional groups of oxine. This chemically modified chitosan is water soluble at low and high pH owing to protonation of the quinoline nitrogen atom and deprotonation of the hydroxyl group of quinolinol, respectively. Consequently, it should be crosslinked in order to make it insoluble in water. However, the crosslinking results in a significant decrease in adsorption capacity due to the formation of chemical bonds at the adsorption sites. In order to overcome this dilemma, it should be crosslinked after it is complexed with metal ions with a high affinity to oxine by the method employed for the preparation of crosslinked copper(II)-complexed chitosan reported in a previous paper (8). The above-mentioned crosslinking method not only ensures high adsorption capacity by protecting the adsorption sites against attack by the crosslinking agents, but is also expected to have high selectivity for the metal ion employed for complexation over other metal ions since the chemical structures of polymer chains "templated" by the metal ions are maintained after crosslinking. Various different types of template polymerization techniques have also been proposed to enhance the selectivity of chelating resins in recent years and have attracted much attention (9, 10). In the present paper a gallium(III)-templated oxine type of chemically modified chitosan (abbreviated Ga-templated oxine chitosan, hereafter) was prepared by the template crosslinking method employing gallium(III) as a template ion because of its high affinity to oxine.

EXPERIMENTAL

Synthesis of Ga-Templated Oxine Chitosan

The route of the template synthesis method of Ga-templated oxine chitosan is shown in Scheme 1. A sample of chitosan, produced and marketed under the trade name Chitosan 95L, was kindly donated by Katokichi



SCHEME 1 Synthetic route of the Ga-templated oxine chitosan.

Co., Kan-onji, Japan, and was used as received without further purification. The degree of deacetylation of the sample chitosan was above 95%. 5-Chloromethyl-8-quinolinol hydrochloride was prepared by stirring 8-quinolinol and formaldehyde in concentrated hydrochloric acid solution with bubbling hydrogen chloride gas according to the method proposed by Kolobielski (11). The oxine type of chemically modified chitosan was prepared by stirring 30 mmol chitosan dissolved in 20 wt% aqueous acetic acid solution together with 60 mmol 5-chloromethyl-8-quinolinol hydrochloride also dissolved in 20 wt% acetic acid solution at 70°C for 72 hours during which 1.43 mol triethylamine was added dropwise as a catalyst. The product was filtered and washed with diethyl ether and ethanol to remove excess 5-chloromethyl-8-quinolinol hydrochloride and triethylamine, and further washed with deionized water to neutral pH to obtain a yellow powder of the final product, the oxine type of chemically modified chitosan.

Since it is soluble in dilute sulfuric acid solution at $\text{pH} < 2.6$, as mentioned earlier, it was crosslinked according to the template synthesis method using gallium(III) as the template metal ion as follows. After stirring 50 mg of oxine type of chitosan in 20 mL sulfuric acid solution containing 60 $\text{mmol}\cdot\text{dm}^{-3}$ gallium(III) nitrate at pH 3.68 in order to give rise to gallium chelate with oxine groups, it was crosslinked with 250 mmol glycerolpolyglycidylether using 8 mmol zinc fluoroborate as a catalyst at 70°C for 120 hours. The powder product was filtered and washed with 50 $\text{mmol}\cdot\text{dm}^{-3}$ sulfuric acid solution to remove gallium to obtain the final product, the Ga-templated oxine chitosan. The Ga-templated oxine chitosan was identified by its infrared spectrum. Characteristic peaks appeared at around 1505 and 1653 cm^{-1} due to the resulting C=C and C=N bonds, respectively. It was confirmed that gallium ion was completely removed from the Ga-oxine chitosan by an electron probe x-ray microanalyzer.

Preparation of Aqueous Metal Solutions

The aqueous metal solutions, except for gallium(III), were prepared by dissolving reagent-grade oxovanadium(IV) sulfate, sodium molybdate(VI), ammonium iron(II) sulfate, indium(III) nitrate, and sulfates of aluminum(III), cadmium(II) and zinc(II) in 50 $\text{mmol}\cdot\text{dm}^{-3}$ sulfuric acid solution. The pH values were adjusted by adding a small amount of sulfuric acid or sodium hydroxide. Gallium(III) solution was prepared by dissolving metallic gallium (purity >99.9999%, kindly donated by Sumitomo Chemical Co.) in heated hydrochloric acid followed by precipitation as gallium(III) hydroxide by pH adjustment. It was then dissolved in sulfuric acid solution in a manner similar to that mentioned earlier.

Batchwise Adsorption of Metal Ions

The adsorption behavior of Ga-templated oxine chitosan for various individual metals from sulfuric acid solution was examined by carrying out batchwise experiments from the point of view of practical application to recovery and recycling of some rare metals; i.e., adsorption of molybdenum(VI), vanadium(IV), and aluminum(III) was examined in relation to the recovery of these metals from spent hydrodesulfurization catalysts (12). Gallium(III), indium(III), cadmium(II), zinc(II), iron(II), and also aluminum(III) were examined in relation to the recovery of the former two kinds of metals from wet process zinc leach residue (13).

About 50 mg of the sieved adsorbents was shaken with a 20-mL aqueous solution containing about 1 mmol·dm^{-3} metal ion in a 50-mL stoppered glass flask immersed in a thermostated water bath maintained at 30°C to attain equilibration except for the experiment to evaluate the maximum adsorption capacity of gallium(III). The initial gallium(III) concentration was varied from 2.2 to 44 mmol·dm^{-3} at initial pH values of 2.04 to 2.09. Initial and equilibrium concentrations of metal ions in the aqueous solutions were determined by using a Seiko model SAS 7500 atomic absorption spectrophotometer for all metal ions except molybdenum(VI) and vanadium(IV), which were determined by a Shimadzu model 1000III ICP-AES spectrometer. The amount of metal ion adsorbed was calculated from the concentrations in the aqueous solutions before and after the adsorption and the weight of dry gel of the adsorbents. The pH of the aqueous solutions was measured by pH meter for pH > 1 and was calculated from the acid concentration determined by neutralization titration and activity coefficient (14) for pH < 1.

The distribution ratio was evaluated as the ratio of amount of adsorbed metal ion per unit kg of dry adsorbent to the metal concentration in the aqueous solution after equilibrium.

Separation of Metals by Using Packed Column

In order to examine the mutual separation by Ga-templated oxine chitosan among some metal ions, separation and recovery of small amounts of gallium and indium from a large amount of zinc were carried out by using a glass column packed with 0.4 g of Ga-templated oxine chitosan as shown in Fig. 1. The diameter and length of the glass column were 1.0 cm and 20.5 cm, respectively, and the temperature was kept at 30°C by use of a water jacket. A feed solution of pH 2 containing 10 ppm gallium(III) and indium(III) together with 900 ppm zinc was passed through the column at a constant feed rate of 7.7 cm^3/h upward from the bottom. The outlet solution was continuously sampled by using a Bio-Rad model

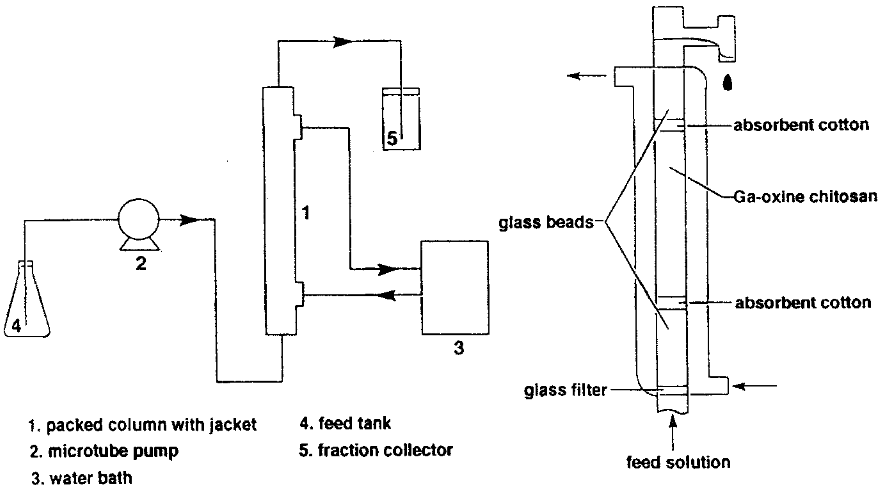


FIG. 1 Schematic diagram of the column packed with Ga-templated oxine chitosan for the separation of metal ions.

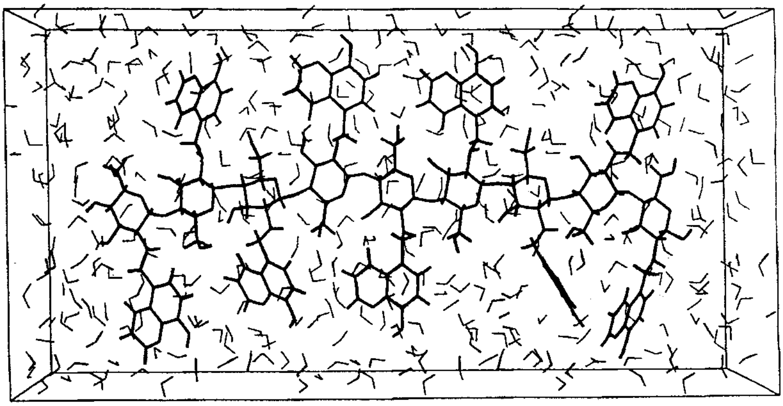
2110 fraction collector. The metal concentration in the inlet and the feed solutions was determined by using a Shimadzu model 1000III ICP-AES spectrometer. After passing 800 B.V. of the feed solution, the loaded metals were eluted from the column by passing 1.0 mol·dm^{-3} sulfuric acid solution through at the same flow rate. The outlet solution was monitored and analyzed in the same manner mentioned above.

RESULTS AND DISCUSSION

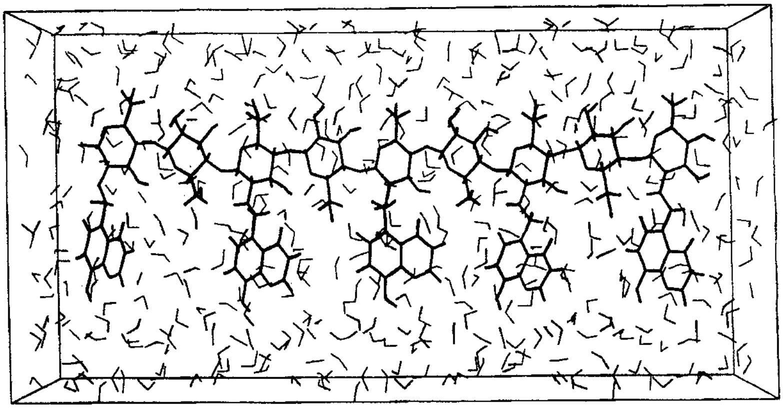
Molecular Mechanics Computation of Conformation of Oxine Type of Chemically Modified Chitosan

Prior to examination of the adsorption behavior of metal ions on Ga-oxine chitosan, the extent of incorporation of oxine groups into the polymer chain of chitosan was evaluated by measuring the number of hydroxyl groups of oxine in the product gel by means of titration with aqueous sodium hydroxide solution. It was evaluated as 30.6%, i.e., one oxine group is incorporated into about 3 glucosamine units. Figures 2(a)–(c)

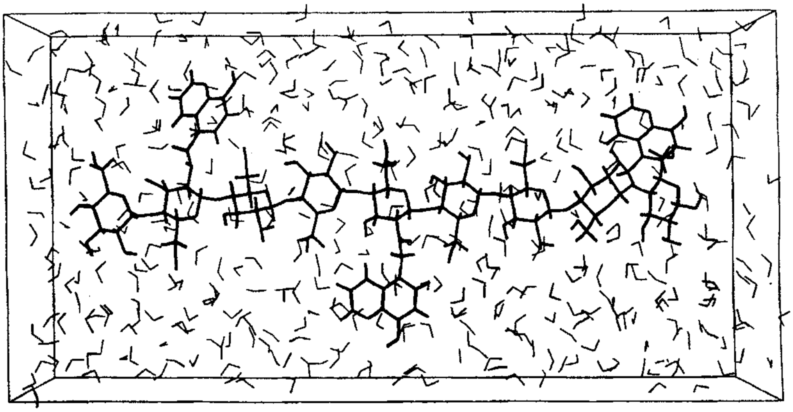
FIG. 2 Configuration of uncrosslinked 9 glucosamine units of chitosan incorporated with oxine groups at the ratio of oxine/glucosamine = 1/1 (a), 1/2 (b), and 1/3 (c), surrounded by 600 water molecules.



(a)



(b)



(c)

show the most stable configuration of 9 uncrosslinked glucosamine units of chitosan incorporated with oxine groups at oxine/glucosamine ratios of 1/1, 1/2, and 1/3, respectively, surrounded by 600 molecules of water, calculated by the molecular mechanic method, CHARMM, using the molecular modeling software, HyperChem Release 4 (Serial No. 519-10006221). For this calculation we used the parameters for all atoms (C, H, N, and O) and bond connections (lengths, bend and torsion angles) available in the literature (15), and we used the TIP3P water model for solvation of solute (16). The heats of formation for the stabilization of these conformation were evaluated as 302, 519, and 204 kJ/9 units, respectively, which are in agreement with the above-mentioned experimental result.

Effect of pH on the Adsorption of Metal Ions

Figure 3 shows plots of the distribution ratio of molybdenum(VI), vanadium(IV), gallium(III), indium(III), aluminum(III), zinc(II), and iron(II) against equilibrium pH in adsorption from sulfuric acid solution on the Ga-templated oxine chitosan. For comparison, Fig. 4 shows similar plots

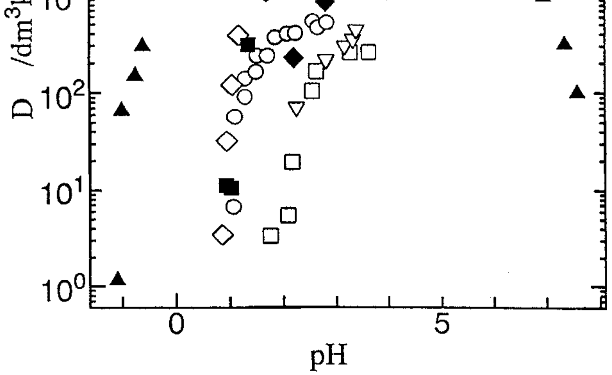


FIG. 3 Plot of distribution ratio (D) against equilibrium pH in the adsorption of molybdenum(VI) (▲), gallium(III) (◇), vanadium(IV) (■), indium(III) (○), zinc(II) (□), iron(II) (◆), and aluminum(III) (▽) from sulfuric acid solution on Ga-templated oxine chitosan.

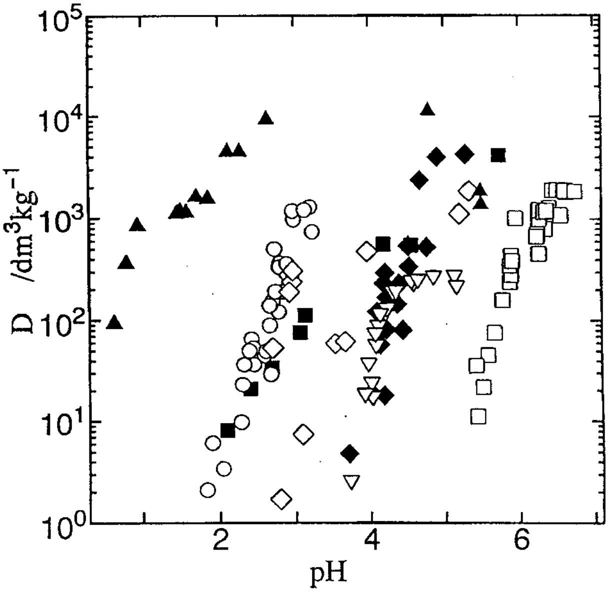


FIG. 4 Plot of distribution ratio (D) against equilibrium pH in the adsorption on original chitosan. The keys are the same with those in Fig. 3.

for these metals in the adsorption on original chitosan. In these figures, plots for $D >$ about 10^4 are excluded since the metal concentration in the aqueous solution after adsorption was too low to be precisely measured. The distribution ratio increases with increasing pH for all metal ions except for molybdenum(VI) at high pH, suggesting that these metal ions are adsorbed according to a cation-exchange mechanism, as expected. The decrease of the adsorption of molybdenum(VI) at high pH is attributable to the formation of unadsorbable anionic species. From a comparison of these two figures it is evident that the pH at which adsorption takes place on Ga-templated oxine chitosan is shifted to lower pH compared with that on original chitosan for all metal ions. This is attributable to a decrease of pK_a of the adsorbent by incorporation of oxine groups into the polymer chain of chitosan. The degree of the shift appears to be the greatest in gallium(III) among the metals examined, which might be attributable to the "template effect" of gallium(III) ion employed as the template or to the higher affinity of the functional group of oxine to gallium(III) than to other metals. The sequence of selectivity of metal adsorption on Ga-templated oxine chitosan appears to be nearly the same as that observed in solvent extraction with oxine (17). For example, although indium(III) is more selectively adsorbed over gallium(III) than on original chitosan, gallium(III) is slightly selectively adsorbed over indium(III) on Ga-templated oxine chitosan.

The experimental results shown in Fig. 3 suggest some possibilities for the practical application of Ga-templated oxine chitosan for the recovery of some rare metals; i.e., the recovery of molybdenum and vanadium from spent hydrodesulfurization catalysts, and the recovery of gallium and indium from wet process zinc leach residue. That is, molybdenum(VI) and vanadium(IV) are selectively adsorbed over aluminum(III) at pH < 2, and gallium(III) and indium(III) are also selectively adsorbed at pH < 2 over zinc(II), aluminum(III), and iron(II).

Maximum Adsorption Capacity of Gallium(III)

Figure 5 shows the relationship between the amount of gallium(III) adsorbed on Ga-templated oxine chitosan and its concentration in the aqueous solution after equilibrium at nearly the same pH. The plots appear to lie on a Langmuir-type adsorption curve and tend to approach a constant value. The maximum adsorption capacity, which was evaluated as 1.17 mol/kg-dry adsorbent, is shown in the figure.

Column Separation

Figure 6 shows the breakthrough profile for the separation of small amounts of gallium(III) and indium(III) from a large amount of zinc(II) at

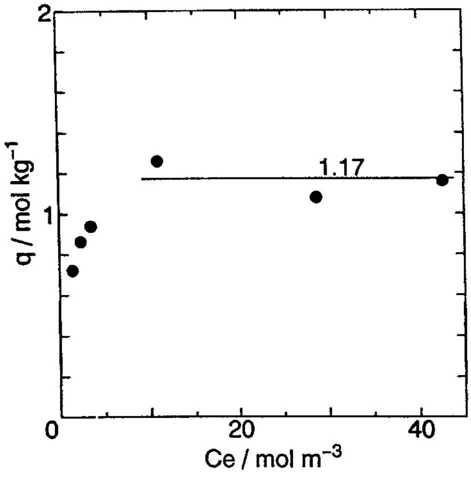


FIG. 5 Relationship between the amount of gallium(III) adsorbed on Ga-templated oxine chitosan and its equilibrium concentration in the aqueous solution at pH 2.

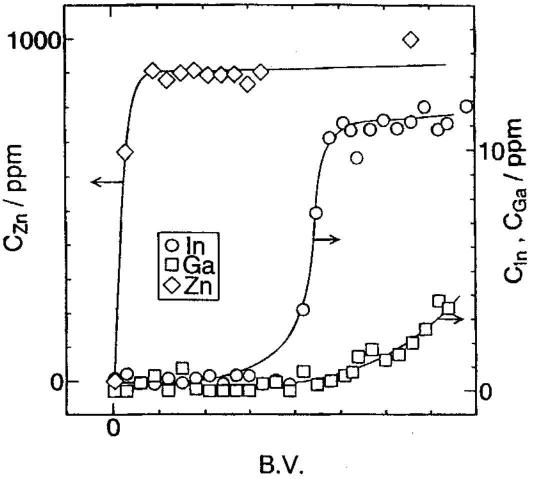


FIG. 6 Breakthrough profile for the separation of gallium(III), indium(III), and zinc(II) using a column packed with Ga-templated oxine chitosan.

pH 2. From this figure it is evident that gallium(III) and indium(III) can be effectively trapped and separated from zinc (as expected from Fig. 3) and, in addition, gallium(III) can be separated from indium(III) even more effectively than expected from Fig. 3.

Figure 7 shows the profile of elution of loaded metal ions from the column. It demonstrates that gallium(III) and indium(III) can be concen-

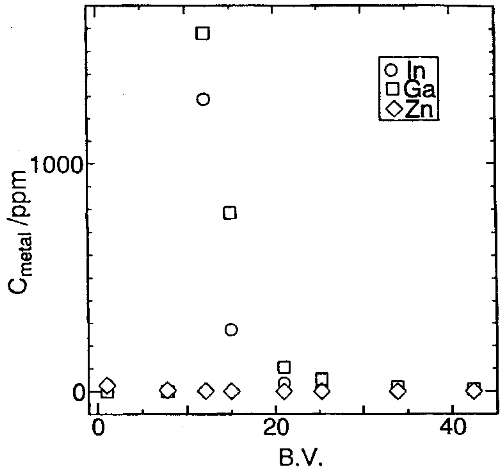


FIG. 7 Elution profile from a packed column of metal-loaded Ga-templated oxine chitosan.

trated as high as several hundred times and free from aluminum contamination.

CONCLUSION

Gallium(III) templated-oxine chitosan was prepared by the template crosslinking method by employing gallium(III) ion as the template ion. The adsorption equilibria of metal ions, i.e., molybdenum(VI), vanadium(IV), indium(III), aluminum(III), zinc(II), iron(II), cadmium(II), and gallium(III), on this adsorbent from dilute sulfuric acid solution was examined to be compared with that on original chitosan. Column separation of gallium(III) and indium(III) from zinc(II) was performed by using a column packed with this chemically modified chitosan.

The following results were obtained:

1. The functional groups of oxine was found to be incorporated into the polymer chain of chitosan at a oxine/glucosamine unit ratio of 1/3, in agreement with what was expected from molecular modeling computation by the molecular mechanics method.
2. The adsorption pH of these metals was lower than that of original chitosan; the degree of the shift was the greatest in gallium(III) among metals examined.
3. The maximum adsorption capacity was evaluated as 1.17 mol/kg-dry adsorbent for gallium(III).
4. This chemically modified chitosan was found to be suitable for the practical application of various recovery processes of rare metals: e.g., recovery of small amounts of indium(III) and gallium(III) from wet process zinc leach residue which contains large amounts of zinc(II), aluminum(III), iron(II) and so on, and that of molybdenum(VI) and vanadium(IV) from spent desulfurization catalysts which contain a large amount of aluminum.
5. The selective adsorption of small amounts of gallium(III) and indium(III) from an excess amount of zinc(II) was confirmed from the breakthrough profile of column separation.

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