Adsorption Behavior of Germanium(IV) on Branched-saccharide Chitosan Derivatives

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Branched-saccharide-chitosan resins and beads selectively adsorbed germanium(IV) from aqueous solutions containing semimetals over the range of weakly acidic to basic media by a batch method. The chitosan derivatives had large adsorption capacities of up to about 2 mmol g⁻¹. On the other hand, by a column method, the chitosan derivatives adsorbed both germanium(IV) and boron. However, when a mixture of germanium(IV) and boron was applied to the column, boron, initially adsorbed on the column, was gradually substituted by germanium(IV), and was finally eluted. The germanium(IV), adsorbed on the column, was almost quantitatively recovered by elution with hydrochloric acid.

Keywords Germanium(IV), chitosan, saccharide, semimetal

Germanium compounds have been widely used in various fields of industry, for example as a catalyst in the production of polyesters. The separation and recovery of germanium(IV) are important because of its high cost. However, germanium(IV) cannot be adsorbed by conventional chelating resins for metal cations, because it dissolves as oxoacid, Ge(OH)₄, and oxoanions, GeO(OH)₃⁻ and GeO₂(OH)₂²⁻, in aqueous solutions.¹ A strongly basic anion-exchange resin can adsorb germanium(IV)², however it has no selectivity for germanium(IV) over anions³⁻⁵. On the other hand, it is well known that germanium(IV) forms complexes with polyol compounds⁶ or saccharides.^{6,7} Therefore, commercially available Sephadex gel¹ and N-methylglucamine resins⁷⁻¹² containing hydroxy groups are used for the preconcentration and separation of germanium(IV). However, the resins do not show high selectivity for germanium(IV) over boron, because they also strongly adsorb boron.^{8,11,13-16}

In previous studies^{17,18} we synthesized 1,2-diol- and 1,3-diol-types polystyrene chelating resins to obtain novel adsorbents with high selectivity for semimetals. The 1,3-diol-type resins adsorbed only boron from semimetals solutions, such as germanium(IV) and tellurium(VI) solutions, in both batch and column methods.¹⁷ The 1,2-diol-type resins selectively adsorbed germanium(IV) over boron, tellurium(VI), arsenic(III) and silicon(IV) in a batch method.¹⁸ However, the adsorption capacities of the diol-types resins for boron and germanium(IV) were still smaller than, or comparable to, that of the commercially available N-methylglucamine resin.^{10,14} On the other hand, chitosan and its derivatives have been widely applied as adsorbents for metal ions¹⁹, and some chitosan derivatives exhibit higher adsorption

capacities for metal ions than conventional chelating resins.^{20,21} However, there have been no studies on the adsorption of semimetals, such as germanium(IV) and boron, on chitosan derivatives, except for a report about a polyaminated chitosan resin.²²

In a preliminary communication²³ we described the branched-saccharide-chitosan resins and beads, prepared from chitosan and saccharides. Germanium(IV) was selectively adsorbed on these resins and beads from aqueous solutions containing semimetals over the range of weakly acidic to basic media by a batch method. The chitosan resins had large adsorption capacities of up to about 2 mmol g⁻¹. The adsorption mechanism is ascribed to complex formation between germanium(IV) and hydroxy groups of the branched saccharide.

In the present study we added discussions on the adsorption rate and isotherms for germanium(IV) and tellurium(VI) on the branched-saccharide-chitosan resins and beads by a batch method, and investigated the adsorption and desorption behavior of germanium(IV), tellurium(VI) and boron on the branched-saccharide-chitosan resins and beads by a column method.

Experimental

Chemicals

Chitosan (trade name: Kimitsu Chitosan LLWP) was donated by Kimitsu Chemical Industries Co., Ltd., Japan. The deacetylated degrees of Kimitsu Chitosan LLWP were determined to be 75-85% by colloidal titration. Chitosan beads (trade name: Chitopearl "Basic" AL-03, particle size 0.3 mm in

diameter) were produced for the crosslinking of chitosan particles with ethylene glycol diglycidyl ether by Fuji Spinning Co., Ltd., Japan.²² Other reagents were reagent or higher grade, and were used without further purifications. All of the aqueous solutions were prepared with distilled and deionized water.

Preparation

Various branched-saccharide-chitosan resins and beads were prepared from chitosan, or chitosan beads, and saccharides, as shown in the preliminary communication.²³

Batch method

About 50 mg of the dried branched-saccharide-chitosan resin or beads and 25 cm³ of the semimetal sample solution were shaken for 24 h in a screwed vial maintained at 25°C. About 1 cm³ of the wet branched-saccharide chitosan beads was also used, when the adsorption rate of semimetal was measured. The initial concentration of semimetal in the sample solution was about 10 mmol dm⁻³, except for in experiments of adsorption isotherms; 0.1 mol dm⁻³ potassium chloride solution was used to maintain a constant ionic strength of the sample solution, except for in experiments of the adsorption rate. The initial pH was adjusted with addition of 0.1-0.5 cm³ diluted hydrochloric acid or aqueous sodium hydroxide. When the adsorption rate of semimetal was measured, ammonium chloride - ammonia buffer was used as the sample solution to maintain a constant pH value. The amounts of adsorbed semimetals were calculated from the differences between the concentrations of semimetals in the aqueous solutions before and after the adsorption, and expressed as mmol per g of the chitosan resins or beads. The concentrations of semimetals were determined using an inductively coupled plasma (ICP) atomic-emission spectrometer (Seiko Instruments Inc., Japan; Model SPS 1200AR). The pH values at equilibrium after 24 h were measured with a pH meter (Horiba, Ltd., Japan; Model F-22).

Column method

The sample solution containing germanium(IV), tellurium(VI) and boron together was loaded on a column (5 mm in diameter), packed with about 1.3 cm³ of the wet branched-saccharide-chitosan resin or beads, at a flow rate of space velocity (SV) about 10 h⁻¹ at room temperature. The concentration of each semimetal in the sample solution was about 1 mmol dm⁻³. An ammonium chloride - ammonia buffer was used as the sample solution to maintain a constant pH value. The elution of the column was carried out by 1 mol dm⁻³ hydrochloric acid at a flow rate of SV about 10 h⁻¹.

In recycle experiments, 77 bed volumes of 1 mmol dm⁻³ germanium(IV) solution, adjusted with a buffer to pH 8.0, were loaded on the branched-mannose

Fig. 1 Effect of the shaking time on the adsorption of germanium(IV) on the branched-mannose-chitosan resin (dried:○) and beads (dried:△)(wet:▲) at pH 9.0-9.1.

chitosan resin column at a flow rate of SV about 10 h⁻¹ at room temperature in each cycle. After being washed with deionized water, germanium(IV) in the column was eluted with 23 bed volumes of 1 mol dm⁻³ hydrochloric acid at a flow rate of SV about 10 h⁻¹. The column was reused after being washed with 1 mol dm⁻³ sodium hydroxide solution and deionized water in recycle experiments. The recovery of germanium(IV) was calculated from the ratio of the amount eluted with the eluent to the amount adsorbed on the column.

Results and Discussion

Adsorption rate and isotherms for germanium(IV) and tellurium(VI) on the branched-saccharide-chitosan resins and beads

Branched-mannose-chitosan resin had the largest adsorption capacity for germanium(IV) from aqueous solution containing tellurium(VI) in the branched-saccharide-chitosan resins and beads, as shown in the preliminary communication²³. In addition, the adsorption rate and isotherms for germanium(IV) and tellurium(VI) on the branched-mannose-chitosan resin and beads by a batch method are discussed as follows.

Figure 1 shows the effect of the shaking time on the adsorption of germanium(IV) on the branched-mannose-chitosan resin and beads at pH 9.0-9.1. The adsorption of germanium(IV) on the wet beads reached equilibrium after 1 h, and the adsorption capacity at equilibrium was about 0.078 mmol cm⁻³ (= 1.7 mmol g⁻¹). For the dried chitosan resin and beads, however, 24 h was required to attain the adsorption equilibrium, and the adsorption capacities at equilibrium were about 2.5 and 1.5 mmol g⁻¹, respectively. Such a decrease in the adsorption rate of germanium(IV) on the dried chitosan resin and beads is attributable to the slower intraparticle

Fig. 2 Adsorption isotherms for germanium(IV)(○) and tellurium(VI)(△) on the branched-mannose chitosan resin at an equilibrium pH of 5.1-7.0 at 25°C.
q: amount adsorbed on the resin.
c: equilibrium concentration in the solution after 24h.

diffusion rate of germanium(IV) in the dried chitosan resin and beads than that in the wet chitosan resin and beads. Similar trends were observed in the adsorption of tellurium(VI), on the branched-mannose chitosan resin at pH 8.3, and germanium(IV), on the branched-galacturonic acid-chitosan resin and beads at pH 8.9-9.1.

Figure 2 shows the adsorption isotherms for germanium(IV) and tellurium(VI) on the branched-mannose chitosan resin at an initial and equilibrium pH of 7.9-8.3 and 5.1-7.0, respectively, at 25°C. The isotherms indicate that germanium(IV) was adsorbed on the resin more than tellurium(VI) in the low semimetal concentration range. Therefore, the separation of germanium(IV) from tellurium(VI) is presumed to be easy in the low semimetal concentration range. Similar trends were observed in the adsorption isotherms for germanium(IV) and tellurium(VI) on the branched-galacturonic acid and -glucuronic acid chitosan resins at an initial and equilibrium pH of 7.8-8.3 and 5.6-7.7, respectively, at 25°C.

Adsorption and desorption behavior of semimetals on and from the branched-saccharide-chitosan resins and beads columns

Figure 3 shows breakthrough curves for germanium(IV), tellurium(VI) and boron in the branched-mannose chitosan resin column at pH 8.5. At first both germanium(IV) and boron were adsorbed on the column. The breakthrough points of germanium(IV) and boron were 140 and 80 bed volumes, respectively. The concentrations of boron in the effluent of 130-300 bed volumes were higher than the initial concentration. This fact means boron, initially adsorbed on the column, was gradually substituted by germanium(IV), and was finally eluted.

Fig. 3 Breakthrough curves for germanium(IV)(○), tellurium(VI)(△) and boron(□) in the branched-mannose chitosan resin column at pH 8.5.

Fig. 4 Elution curves for germanium(IV)(○), tellurium(VI)(△) and boron(□) with 1 mol dm⁻³ hydrochloric acid in the branched-mannose chitosan resin column.

This substitution is due to the high separation factor of germanium(IV) to boron for the competitive adsorption of the branched-mannose chitosan resin by a batch method.²³ On the other hand, tellurium(VI) leaked immediately in spite of the low separation factor of germanium(IV) to tellurium(VI) for the competitive adsorption of the branched-mannose chitosan resin by a batch method.²³ When only tellurium(VI) was loaded on the column, it did not leak immediately. Therefore, the adsorption of germanium(IV) and boron on the column seems to cause the leakage of tellurium(VI).

Figure 4 shows the elution curves for germanium(IV), tellurium(VI) and boron with 1 mol dm⁻³ hydrochloric acid in the branched-mannose chitosan resin column. Since no tellurium(VI) was adsorbed on the column, it was not eluted. A small amount of boron was eluted, because most of boron was substituted by germanium(IV). After all the elution of the column with hydrochloric acid mainly gave germanium(IV). Most of germanium(IV) was

Table 1 Elution of germanium(IV), adsorbed on the branched-mannose chitosan resin column, with 1 mol dm⁻³ hydrochloric acid

Cycle No.	Adsorbed ^a Ge(IV)/ mg	Eluted ^b Ge(IV)/ mg	Recovery/ %
1	7.24	6.92	95.7
2	7.24	6.58	90.9
3	7.86	7.27	92.5

a. Sample volume was 77 bed volumes of 1 mmol dm⁻³ germanium(IV) solution at pH 8.0

b. Eluent volume was 23 bed volumes of 1 mol dm⁻³ hydrochloric acid.

eluted in the initial 10 bed volumes of the effluent.

Similar trends were observed in the adsorption and desorption of germanium(IV), tellurium(VI) and boron on the branched-glucuronic acid chitosan resin, the branched-xylose-chitosan resin and beads columns. The breakthrough points of germanium(IV), in the columns with almost same bed volume, decreased in the order of the branched-mannose chitosan resin > the branched-glucuronic acid chitosan resin ≥ the branched-xylose chitosan resin > the branched-xylose chitosan beads. This order is the same as that of the adsorption capacities for germanium(IV) by a batch method.²³ For the branched-xylose-chitosan resin and beads columns, most of germanium(IV) was eluted in less than 10 bed volumes of the effluent. However, for the branched-glucuronic acid chitosan resin column, 20 bed volumes of the effluent were required to elute most of germanium(IV) with hydrochloric acid.

The cycle of adsorption, washing, elution and washing steps was repeated 3 times in order to check the reproducibility of the branched-mannose chitosan resin column system in the adsorption and desorption of germanium(IV). The results are shown in Table 1. The germanium(IV), adsorbed on the column, was almost quantitatively eluted with hydrochloric acid in each cycle. That is, selective separation and a considerable concentration effect of germanium(IV) were achieved by utilizing the branched-mannose chitosan resin column.

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