Selective Separation of Germanium(IV) by Iminodiacetic Acid-Type Chitosan Chelating Resin

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An iminodiacetic acid-type chitosan chelating resin selectively adsorbed germanium(IV) from aqueous solutions over the range of strongly acidic to weakly basic media. The adsorption capacity of the chitosan resin for germanium(IV) was about 1 mmol g⁻¹ in acidic media. The selective separation of germanium(IV) from tellurium(VI) and boron was achieved with a column method using the chitosan resin. The breakthrough points of germanium(IV) in the chitosan resin columns were about 70 bed volumes over the range of strongly acidic to weakly basic media. The germanium(IV) adsorbed on the column was almost quantitatively recovered by elution with aqueous sodium hydroxide. On the other hand, it was difficult to separate germanium(IV) from tellurium(VI) using a column of the polyamine-type chitosan chelating resin.

Keywords  Germanium, chitosan, iminodiacetic acid-type chelating resin, semimetal, polyamine-type chelating resin

In general, mutual separation of semimetals, such as germanium(IV), tellurium(IV) and boron, is difficult because of their similar behavior in aqueous solutions. Therefore, in previous studies¹,² 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.¹ The 1,2-diol-type resins selectively adsorbed germanium(IV) over boron, tellurium(VI), arsenic(III) and silicon(IV).² However, the adsorption capacities of the diol-type resins for boron and germanium(IV) were still smaller than, or comparable to, that of the commercially available N-methylglucamine resin.³,⁴ On the other hand, chitosan and its derivatives have been widely applied as adsorbents for metal ions⁵, and some chitosan derivatives exhibit larger adsorption capacities for metal ions than conventional chelating resins.⁶,⁷ However, there have been no studies on the adsorption of semimetals, such as germanium(IV), tellurium(VI) and boron, on chitosan derivatives, except for a report⁸ about a polyamine-type chitosan resin.

In the present study we investigated the adsorption behavior of germanium(IV), tellurium(IV) and boron on commercially available chitosan chelating resins by a batch method, since chitosan resins are expected to have large adsorption capacities because of the higher hydrophilicity of chitosan resins than that of polystyrene resins. Also, we describe the adsorption and desorption behavior of the semimetals on the chitosan resins by a column method.

**Experimental**

**Chemicals**

Chitosan chelating resins (particle size 0.3 mm in diameter) were an iminodiacetic acid-type (CI) (trade name: Chelate Chitopearl CI-03)⁹, a polyamine-type (CS) (trade name: Chelate Chitopearl CS-03), an aromatic carboxylic acid-type (CT) (trade name: Chelate Chitopearl CT-03)¹⁰ and an amino-type (AL) (trade name: Chitopearl “Basic” AL-03) produced by Fuji Spinning Co., Ltd., Japan. An iminodiacetic acid-type polystyrene chelating resin (CR10) (trade name: Diaion CR10), a polyamine-type polystyrene chelating resin (CR20) (trade name: Diaion CR20), a polyamine-type polystyrene ion-exchange resin (WA20) (trade name: Diaion WA20), of which the total ion-exchange capacity was more than 2.5 mequiv. cm⁻³, produced by Mitsubishi Chemistry Co., Ltd., Japan, were used for comparisons. An iminodiacetic acid-type agarose chelating resin (SFF) (trade name: Chelating Sepharose Fast Flow) produced by Pharmacia Biotech Co., Sweden, was also used for a comparison. Other reagents were of reagent or higher grade, and were used without further purifications. All of the aqueous solutions were prepared with distilled and deionized water.

**Batch method procedure**

About 50 mg of the dried (at 40°C for 4 h under
reduced pressure) chitosan chelating resin and 25 cm³ of the semimetal sample solution, in which two kinds of semimetals, such as germanium(IV), tellurium(VI), boron, arsenic(III), arsenic(V), selenium(IV) and selenium(VI), were contained for competitive adsorption experiments, were shaken in a screwed vial maintained at 25°C for 24 h under standard conditions. About 1 cm³ of the wet chitosan chelating resin 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 hydrochloric acid or aqueous sodium hydroxide. When the adsorption rate of semimetal was measured, potassium hydrogen phthalate-potassium hydroxide buffer or 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 chelating resins. The concentrations of semimetals were determined using an inductively coupled plasma atomic-emission spectrometer (Seiko Instruments Inc., Japan; Model SPS 1200AR). The pH values at equilibrium after 24 h of shaking were measured with a pH meter (Horiba, Ltd., Japan; Model F-22).

Column method procedure

The sample solution, containing semimetals, such as germanium(IV), tellurium(VI) and boron, was loaded on a column (5 mm in diameter), packed with about 1.8 cm³ of the wet chitosan chelating resin, at a flow rate of space velocity (SV) about 10 h⁻¹ at room temperature. The concentration of semimetals in the sample solution was about 1 mmol dm⁻³. An ammonium chloride-ammonia buffer, a potassium hydrogen phthalate-potassium hydroxide buffer or a sodium acetate-hydrochloric acid buffer was used as the sample solution to maintain a constant pH value. In recycle experiments, 83 bed volumes of 1 mmol dm⁻³ germanium(IV) solution, adjusted with a buffer to pH 8.2, were loaded on the iminodiacetic acid-type chitosan chelating resin (CI) 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 11 bed volumes of 1 mol dm⁻³ sodium hydroxide solution at a flow rate of SV about 10 h⁻¹. The column was reused after being washed with 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

Effect of pH on the adsorption of semimetals on the chitosan chelating resins

Figure 1 shows the effect of the pH on the adsorption of germanium(IV), tellurium(VI) and boron on the polyamine-type chitosan chelating resin (CS). The adsorption capacities of the polyamine-type chitosan resin (CS) for germanium(IV) and tellurium(VI) reached maximum values (about 2.0 and 1.8 mmol g⁻¹, respectively) at around pH 8–9. However, boron was hardly adsorbed on the polyamine-type chitosan resin (CS) over the whole pH range. This trend, as shown in Fig. 1, was similar to that for a strongly basic ion-exchange resin.11,12 The effect of the pH on the adsorption of germanium(IV) and tellurium(VI) on the polyamine-type polystyrene ion-exchange resin (WA20) was similar to that on the polyamine-type chitosan resin (CS). The maximum adsorption capacities of the polyamine-type polystyrene ion-exchange resin (WA20) for germanium(IV) and tellurium(VI) were about 0.5 and 1 mmol g⁻¹, respectively, and were smaller than those of the polyamine-type chitosan resin (CS). On the other hand, the polyamine-type polystyrene chelating resin (CR20), which has a small adsorption capacity, did not adsorb germanium(IV) and tellurium(VI) over the whole pH range. These results suggest that the adsorption mechanism of germanium(IV) and tellurium(VI) on the polyamine-type chitosan resin (CS) having polyethyleneimino groups8, which were moderately basic ion-exchange groups, is mainly ascribed to ion-exchange reaction11,12 over the range of acidic to weakly basic media.

Figure 2 shows the effect of the pH on the adsorption of germanium(IV), tellurium(VI) and boron on the iminodiacetic acid-type chitosan chelating resin (CI). About 1 mmol g⁻¹ of germanium(IV) was adsorbed on the iminodiacetic acid-type chitosan resin (CI) over the range of strongly acidic to weakly basic media, and was
comparable to the adsorption capacities of the 1,2-diol-type polystyrene resin for germanium(IV). In a strongly basic medium, only a small amount of germanium(IV) was adsorbed on the iminodiacetic acid-type chitosan resin (CI). However, tellurium(VI) and boron were hardly adsorbed on the iminodiacetic acid-type chitosan resin (CI) over the whole pH range. On the other hand, the iminodiacetic acid-type polystyrene chelating resin (CR10) and the iminodiacetic acid-type agarose chelating resin (SFF) did not adsorb germanium(IV) over the whole pH range. These results suggest that the adsorption of germanium(IV) is not due to only chelation between the iminodiacetic acid group and germanium (IV). Since the iminodiacetic acid-type chitosan resin (CI) also has polyamine groups, both the iminodiacetic acid and polyamine groups may participate in the adsorption of germanium(IV). However, the details concerning the adsorption mechanism of germanium(IV) on the iminodiacetic acid-type chitosan resin (CI) are not presently clear.

In addition, the aromatic carboxylic acid-type (CT) and the amino-type (AL) chitosan chelating resins hardly adsorbed any semimetals, such as germanium(IV), tellurium(VI), and boron, over the whole pH range.

On the basis of these results, experiments using the iminodiacetic acid-type (CI) and the polyamine-type (CS) chitosan chelating resins were carried out.

Adsorption rate of germanium(IV) and tellurium(VI) on the chitosan chelating resins

Figure 3 shows the effect of the shaking time on the adsorption of germanium(IV) on the wet iminodiacetic acid-type chitosan chelating resin (CI) at pH 4.6. The adsorption of germanium(IV) reached equilibrium after 5 h, and the adsorption capacity at equilibrium was about 0.17 mmol cm\(^{-3}\) (≈0.83 mmol g\(^{-1}\)). For the dried iminodiacetic acid-type chitosan resin (CI), however, 24 h was required to attain the adsorption equilibrium at pH 9.0. Such a decrease in the adsorption rate of germanium(IV) on the dried chitosan resin (CI) is attributable to the slower intraparticle diffusion rate of germanium(IV) in the dried chitosan resin than that in the wet chitosan resin.

Similar trends were observed in the adsorption of germanium(IV) and tellurium(VI) on the polyamine-type chitosan chelating resin (CS). In the cases of the wet and dried polyamine-type chitosan resins (CS), the adsorption reached equilibrium after 5 and 24 h, respectively, at pH 9.0 - 9.4.

Adsorption isotherms for germanium(IV) and tellurium(VI) on the chitosan chelating resins

Figures 4 and 5 show the adsorption isotherms for germanium(IV) and tellurium(VI) on the iminodiacetic acid-type chitosan chelating resin (CI) at an equilibrium pH of 6.4 - 7.7 and the polyamine-type chitosan chelating resin (CS) at an equilibrium pH of 8.4 - 8.8, respectively, at 25°C. For the iminodiacetic acid-type chitosan resin (CI) germanium(IV) was adsorbed more than tellurium(VI) over the entire semimetal concentration range. On the other hand, for the polyamine-type chitosan resin (CS) the amounts of adsorbed germanium(IV) were comparable to those of adsorbed tellurium(VI) in the high semimetal concentration range. Therefore, the separation of germanium(IV) from tellurium(VI) in the polyamine-type chitosan resin (CS) is presumed to be difficult in the high semimetal concentration range.

Separation factors of germanium(IV) to the other semimetals for the competitive adsorption of semimetals on the chitosan chelating resins

Table 1 shows the separation factors of germanium (IV) to the other semimetals for the competitive adsorption of semimetals on the iminodiacetic acid-type
chitosan chelating resin (CI) at an initial pH of about 8 and an equilibrium pH of 6.4–7.8. An initial pH of about 8 was selected to compare with the competitive adsorption of semimetals on the polyamine-type chitosan chelating resin (CS). The separation factor ($\alpha$) is defined as $\alpha = K_{dl}/K_{d2}$, where $K_{dl}$ and $K_{d2}$ represent the distribution coefficient [the semimetal concentration on the chitosan resin (mg kg$^{-1}$)/that in the aqueous solution (mg dm$^{-3}$) after the adsorption] of germanium(IV) and the other semimetal, respectively. The separation factors of germanium(IV) to tellurium(VI), boron, arsenic (III), arsenic(V), selenium(IV) and selenium(VI) were much larger. That is, small amounts of tellurium(VI), boron, arsenic(III), arsenic(V), selenium(IV) and selenium(VI) were adsorbed on the iminodiacetic acid-type chitosan resin (CI) due to competitive adsorption with germanium(IV). In addition, tellurium(IV) was not examined because of the production of a precipitate around neutral media. Consequently, the iminodiacetic acid-type chitosan resin (CI) was found to be a highly selective adsorbent for germanium(IV).

On the other hand, the separation factor of germanium(IV) to tellurium(VI) on the polyamine-type chitosan chelating resin (CS) at an initial pH of about 8 was nearly 1, as shown in Table 1. That is, the amount of adsorbed germanium(IV) was comparable to that of adsorbed tellurium(VI) for the competitive adsorption on the polyamine-type chitosan resin (CS).

### Table 1: Separation factors of germanium(IV) to the other semimetals for the competitive adsorption of semimetals on chitosan chelating resins

<table>
<thead>
<tr>
<th>Chitosan chelating resin</th>
<th>Equilibrium pH</th>
<th>Separation factor</th>
<th>Ge(IV)</th>
<th>Te(IV)</th>
<th>B(III)</th>
<th>As(III)</th>
<th>As(V)</th>
<th>Se(IV)</th>
<th>Se(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iminodiacetic acid-type (CI)</td>
<td>6.4–7.8</td>
<td>5.4</td>
<td>1.0</td>
<td>180</td>
<td>16</td>
<td>37</td>
<td>190</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td>Polyamine-type (CS)</td>
<td>9.2</td>
<td>0.95</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
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Adsorption behavior of semimetals on the chitosan chelating resins columns

Figure 6 shows breakthrough curves for germanium(IV), tellurium(VI) and boron in the polyamine-type chitosan chelating resin (CS) column at pH 8.5. Boron leaked immediately, as predicted from Fig. 1, and the concentration of boron in the effluent fraction rapidly reached the initial concentration. Although tellurium(VI) was adsorbed on the column, it began to leak, even in initial effluent fractions. Germanium(IV) was also adsorbed on the column, but the breakthrough point was only 16 bed volumes. Therefore, the separation of germanium(IV) from tellurium(VI) by the polyamine-type chitosan resin (CS) column is difficult, as predicted in Fig. 5 and Table 1.

On the other hand, Fig. 7 shows breakthrough curves for germanium(IV), tellurium(VI) and boron in the
iminodiacetic acid-type chitosan chelating resin (CI) column at pH 8.4. Tellurium(VI) and boron leaked immediately, as predicted from Fig. 2, and the concentrations of tellurium(VI) and boron in the effluent fractions rapidly reached the initial concentrations. Germanium(IV) was adsorbed on the column; the breakthrough point of germanium(IV) was 70 bed volumes. Similar breakthrough curves were obtained at pH 0.3 and 4.5. Therefore, the iminodiacetic acid-type chitosan resin (CI) column can selectively adsorb germanium(IV) over tellurium(VI) and boron over the range of strongly acidic to weakly basic media.

Figure 8 shows the elution curves for germanium(IV), tellurium(VI) and boron with aqueous sodium hydroxide in the iminodiacetic acid-type chitosan chelating resin (CI) column. Since no tellurium(VI) and boron were adsorbed on the column, they were not eluted. Most of germanium(IV) was eluted in the initial 5 bed volumes of the effluent. The cycle of adsorption, washing, elution and washing steps was repeated 3 times in order to check the reproducibility of the column system. The results are shown in Table 2. The germanium(IV) adsorbed on the column was almost quantitatively eluted with aqueous sodium hydroxide in each cycle. That is, selective separation and a considerable concentration effect of germanium(IV) were achieved by utilizing the iminodiacetic acid-type chitosan resin (CI) column. Therefore, this column system can be applied to the preconcentration of ultratrace germanium(IV) in natural water and industrial waste water.
References


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