



Adsorption behavior of uranium(VI) and other ionic species on cross-linked chitosan resins modified with chelating moieties

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ABSTRACT

Cross-linked chitosan resins with catechol (catechol-type chitosan, type 1 and type 2), iminodiacetic acid (IDA-type chitosan), iminodimethylphosphonic acid (IDP-type chitosan), phenylarsonic acid (phenylarsonic acid-type chitosan), or serine (serine-type chitosan) were prepared for the collection and concentration of uranium(VI). The adsorption behavior of U(VI) and other ionic species, such as metal ions and oxo-acid ions, on the cross-linked chitosan (base material) and chitosan resins modified with chelating moieties was examined using a column procedure. Especially, the catechol-type chitosan (type 2) adsorbed U(VI) at pH 2–7, and selectively collected U(VI) at acidic pH regions by forming a stable chelate with hydroxyl groups of catechol moiety introduced to the chitosan. Also, the adsorption properties of cationic and anionic species present in aquatic media were elucidated. The adsorption ability for U(VI) was in the order: catechol-type chitosan (type 2) > serine-type chitosan > phenylarsonic acid-type chitosan > the others. The catechol-type chitosan (type 2) was useful for the collection and concentration of uranium(VI).

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1. Introduction

Uranium must be determined for evaluating and estimating the uranium behavior in aquatic samples. Seawater, river water, and tap water contain uranium at several ppb level (1 ppb = 1 $\mu\text{g L}^{-1}$), several-ten ppt level (1 ppt = 1 ng L^{-1}), and several ppt level. Some analytical techniques have been used for the uranium determination, whereas the methods generally are not sensitive enough [1,2]. An ICP-OES is one of the powerful analytical techniques for its determination but LOD is usually within the lower $\mu\text{g L}^{-1}$ range. Therefore, the effective preconcentration technique for uranium determination is necessary prior to ICP-OES measurement. And then, the deposition of matrix constituents, such as Na, K, Mg, and Ca, in seawater and river water on the torch and nebulizer may seriously affect the measurement accuracy. In order to overcome such problems, solid-phase extraction procedures have been developed and applied to the effective pretreatment prior to trace analysis [3–12]. Some researchers have reported on solid materials modified with chelating moieties, such as succinic acid, maleic acid, *o*-vaniline

semicarbazone, and 8-hydroxyquinoline, which adsorb the trace U(VI) only over narrow pH regions [4–8]. Also, commercially available chelating resins with dipentylphosphonate (DPPP) and anion-exchange resins, such as UTEVA and Dowex 1-X8, could adsorb uranium(VI) only in concentrated acidic solutions, and these resins then produced a large amount of acidic wastes, which was one of the serious problems from environmental point view [9–12].

In our previous work, various kinds of chitosan-based chelating resin were synthesized for the collection and concentration of trace elements in aquatic samples. The adsorption rate of ionic species on chitosan resins is faster in aquatic media than that on synthetic base materials, such as polystyrene–divinylbenzene, polyethylene, and polyurethane, which is due to the hydrophilicity of chitosan itself [13]. Also, chitosan resins with different types of chelating moiety have been developed for the uranium collection [13–18], whereas these adsorption properties were not discussed each other.

In this study, the adsorption behavior of uranium(VI) and other ionic species on the cross-linked chitosan (base material) and chitosan-based chelating resins with catechol (catechol-type chitosan of type 1 and type 2), iminodiacetic acid (IDA-type chitosan), iminodimethylphosphonic acid (IDP-type chitosan), phenylarsonic acid (phenylarsonic acid-type chitosan), and serine (serine-type chitosan) were discussed in detail.

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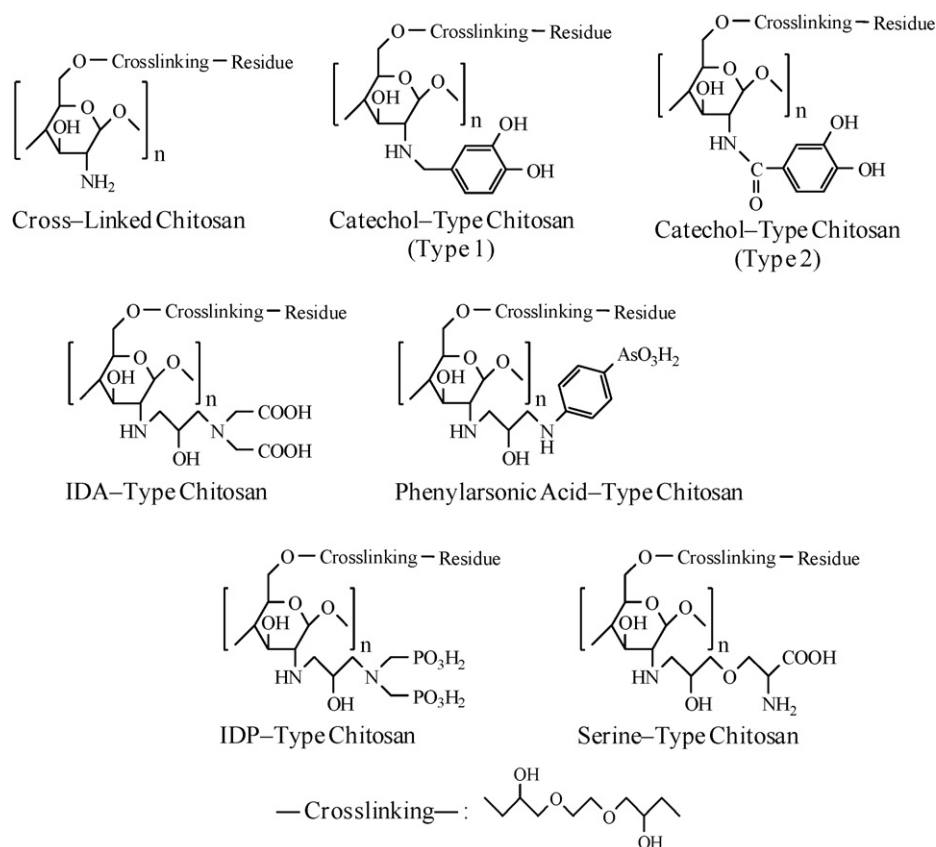


Fig. 1. Chemical structures of cross-linked chitosan and chitosan resins functionalized with chelating moieties.

2. Experimental

2.1. Instruments

An ICP-MS system, which was a Model SPQ 8000H (Seiko Instruments, Chiba, Japan), was used for measuring the elements after the batchwise column procedure. The IR spectra were taken by KBr pellet method using an FT/IR-4100 spectrometer (JASCO Co., Tokyo, Japan).

2.2. Reagents

The cross-linked chitosan (base material) and chitosan resins modified with catechol (catechol-type chitosan of type 1 and type 2), iminodiacetic acid (IDA-type chitosan), iminodimethylphosphonic acid (IDP-type chitosan), phenylarsonic acid (phenylarsonic acid-type chitosan), and serine (serine-type chitosan) were synthesized in a similar manner to our previous work [13–19]. These chitosan resins were characterized by considering their IR spectra. The chitosan-based chelating resins examined in this work are shown in Fig. 1. The chitosan (Tokyo Kasei Co. Ltd., Tokyo, Japan) used as a base material was in a flake form, whose deacetylated degree was about 80%. All other reagents used for the synthesis of chitosan resins were of analytical reagent grade.

The stock standard solutions of analytical standard were prepared by diluting several kinds of single-element standard solution for atomic-absorption spectrometry (1000 mg L^{-1}) purchased from Wako Pure Chemicals (Osaka, Japan) and multi-element standard solution for ICP-MS purchased from Spex CertiPrep Inc. (Metuchen, New Jersey, USA). These stock solutions were diluted by weight just before a column procedure with 0.1 mol L^{-1} nitric acid to give $10 \mu\text{g L}^{-1}$ of each element. Ultrapure-grade nitric acid (60%; density,

1.38 g mL^{-1}), which was purchased from Kanto Chemicals (Tokyo, Japan), was diluted with water. Acetic acid (minimum 96%) and ammonia water (29%) used for preparing an ammonium acetate solution were of an electronic industrial reagent grade, which were purchased from Kanto Chemicals (Tokyo, Japan). Ultrapure water (resistivity higher than $18.3 \text{ M}\Omega \text{ cm}^{-1}$), prepared by an Elix 3/Milli-Q Element system (Nihon Millipore, Tokyo, Japan), was used throughout.

2.3. Batchwise column procedure

The column procedure was similar to our previous work [18]. Each chitosan resin was cleaned up to remove any residual metallic impurities as follows. The wet resin (20 mL) was transferred to a plastic beaker (100 mL) with 2 mol L^{-1} nitric acid (80 mL). After the resin was carefully stirred at a low speed for 6 h, it was filtered and rinsed with water. The wet resin was packed in a polypropylene mini-column (volume: 1 mL; size: 5.0 mm i.d. \times 50 mm length), which was purchased from Muromachi Chemicals (Kyoto, Japan). It was used for examining the adsorption behavior of ionic species as follows. For washing, each 10 mL of 1 mol L^{-1} nitric acid and water were passed through the column. Then, 5 mL of a conditioning solution (pH 1–2, 0.1 mol L^{-1} and 0.01 mol L^{-1} nitric acid; pH 3–7, 0.5 M ammonium-acetate solution) was passed through it for pH adjustment. For adsorbing ionic species such as uranium(VI) and other ions, a sample solution (10 mL), whose pH was adjusted with the conditioning solution, was passed through the column. And, a 5 mL aliquot of a rinsing solution (pH 1–2, 0.1 mol L^{-1} and 0.01 mol L^{-1} nitric acid; pH 3–7, 0.2 mol L^{-1} ammonia-acetate solution) and a 5 mL portion of water were then passed through each column for removing and rinsing the remaining components from the column. Finally, for eluting and recovering ionic species adsorbed on the

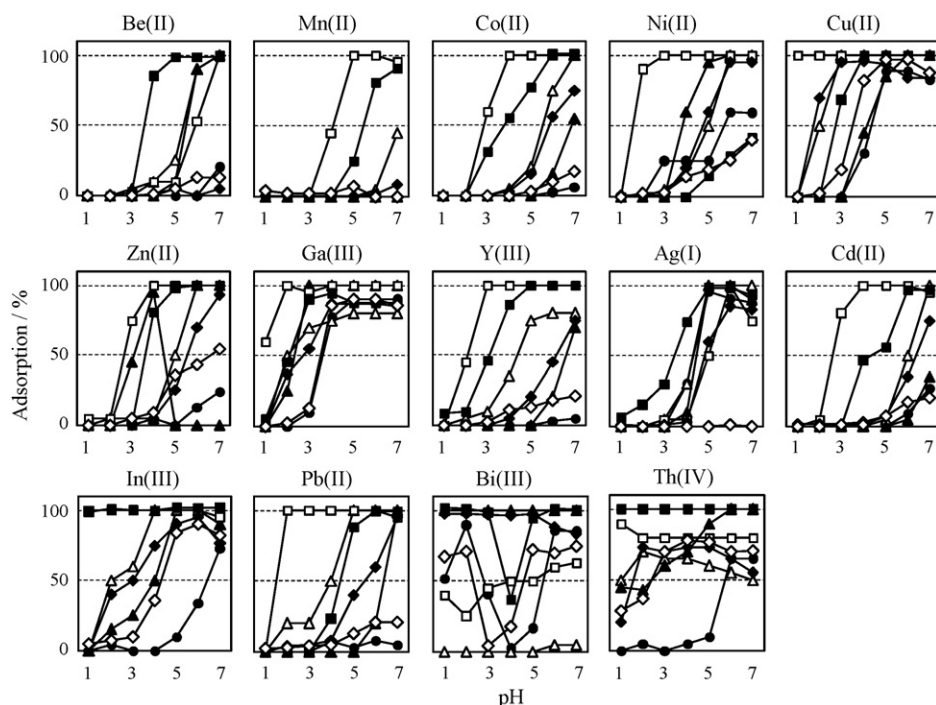


Fig. 2. Adsorption behavior of metals at pH 1–7 on chitosan resins. Sample, 10 mL; concentration of each element, $10 \mu\text{g L}^{-1}$; column, 1 mL; eluent, 10 mL of 1 mol L^{-1} nitric acid. (●) Cross-linked chitosan; (△) catechol-type chitosan (type 1); (▲) catechol-type chitosan (type 2); (□) IDA-type chitosan; (■) IDP-type chitosan; (◇) phenylarsonic acid-type chitosan; (◆) serine-type chitosan.

resin, each 10 mL portion of 1 mol L^{-1} nitric acid was passed through the column. The ionic species in each effluent were measured by ICP–MS. Throughout all of the column procedure, the flow rate was maintained at about 1 mL min^{-1} .

3. Results and discussion

3.1. Adsorption behavior of metals on chitosan resins

The adsorption capacities of Cu(II), which could form stable chelates with various kinds of chelating moiety, on chitosan resins were as follows: catechol-type chitosan (type 1), $0.08 \text{ mmol mL}^{-1}$; catechol-type chitosan (type 2), $0.14 \text{ mmol mL}^{-1}$; IDA-type chitosan, $0.14 \text{ mmol mL}^{-1}$; IDP-type chitosan, $0.04 \text{ mmol mL}^{-1}$; phenylarsonic acid-type chitosan, $0.02 \text{ mmol mL}^{-1}$; serine-type chitosan, $0.08 \text{ mmol mL}^{-1}$. It might be caused by the introduction efficiency of chelating moieties to the chitosan, and the adsorption mechanism such as chelating and ion-exchange mechanism. These capacities were in large excess to the amount ($10 \mu\text{g L}^{-1}$) of each element, which was examined in the following experiments. The adsorption properties of (1) metals, (2) lanthanoids, (3) oxo-acids, and (4) uranium on the chitosan resins were examined by the column procedure.

Fig. 2 shows the adsorption behavior of metal ions, such as Be(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Y(III), Ag(I), Cd(II), In(III), Pb(II), Bi(III), and Th(IV), at pH 1–7, which are existing as cationic species in aqueous solution. Almost all metal ions adsorbed on chitosan resins could be recovered with an eluent (1 mol L^{-1} , 10 mL) thoroughly. Chitosan resins with chelating moieties could adsorb metal ions more effectively than the cross-linked chitosan (base material). It might be caused by modifying the cross-linked chitosan with chelating moieties. IDA-type chitosan (□) could adsorb various kinds of metal ion, such as Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Y(III), Cd(II), In(III), Pb(II) and Th(IV), at wider pH regions than the other types of chitosan resin. The IDA moiety, $-\text{N}(\text{CH}_2\text{COOH})_2$, could form more stable chelates with these metal ions than the other

chelating moieties. Also, IDP-type chitosan (■) could adsorb many metal ions at wide pH regions. Especially, In(III) and Th(IV) could be adsorbed at wider pH region from 1 to 7. The metal ions except for Th(IV) adsorbed on the IDP-type chitosan were readily eluted with 1 mol L^{-1} nitric acid, whereas Th(IV) was not eluted even with 6 mol L^{-1} nitric acid or 6 mol L^{-1} hydrochloric acid. The adsorption mechanism of Th(IV) on IDP-type chitosan might be different from that of other metal ions. On the other hand, the adsorption behavior of metal ions on the catechol-type chitosan (type 1 and type 2), phenylarsonic acid-type chitosan, and serine-type chitosan, were different from that on the IDA-type chitosan and IDP-type chitosan. Chitosan resin with the catechol, phenylarsonic acid, and serine moieties, did not adsorb the metal ions effectively. The chelating moieties, such as iminodiacetic acid $\{\text{IDA}, -\text{N}(\text{CH}_2\text{COOH})_2\}$ and iminodimethylphosphonic acid $\{\text{IDP}, -\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2\}$ might form more stable chelates with such metal ions than the catechol, phenylarsonic acid, and serine moieties.

3.2. Adsorption behavior of lanthanoids on chitosan resins

Fig. 3 shows the adsorption behavior of lanthanoids, which exist as cationic species Ln(III) in aqueous solution, on chitosan resins at pH from 1 to 7. IDA-type chitosan could adsorb lanthanoids at wider pH regions than the other types of chitosan resin. The IDA moiety might form more stable chelates with Ln(III) than the other chelating moieties, such as IDP, catechol, phenylarsonic acid, and serine. Also, IDP-type chitosan and catechol-type chitosan (type 1) adsorb Ln(III) at pH 5–7 more effectively than the other types of chitosan resin except for IDA-type chitosan. On the other hand, cross-linked chitosan (base material) could not adsorb Ln(III). It might be caused by the modification of cross-linked chitosan with chelating moieties, such as IDA, catechol, and IDP, which form the stable chelate with Ln(III). The adsorption ability of chitosan resins for lanthanoids was the following order; IDA-type chitosan > IDP-type chitosan = catechol-type chitosan (type 1) > the other types of chitosan resin.

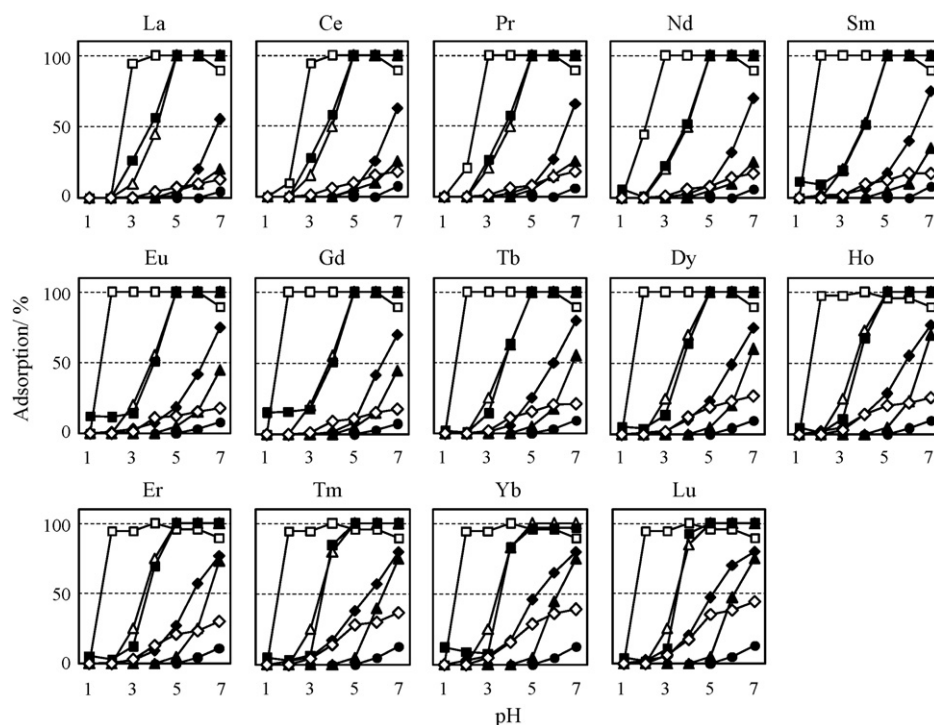


Fig. 3. Adsorption behavior of lanthanoids at pH 1–7 on chitosan resins. The experimental conditions and symbols are the same as in Fig. 2.

3.3. Adsorption behavior of oxo-acids on chitosan resins

Fig. 4 shows the adsorption behavior of oxo-acids, such as V(V), Ge(IV), Mo(VI), and W(VI), on chitosan resins. The adsorption of oxo-acids was quite different from that of metals and lanthanoids described above. Chitosan resins adsorbed such oxo-acids at wide pH regions. Especially, vanadium was adsorbed on IDA-type chitosan at pH 1–7 and on catechol-type chitosan at pH 3–7, and then Ge(IV) was adsorbed on IDP-type chitosan resin at pH 3–7. Oxo-acid species, such as V(V), Ge(IV), Mo(VI) and W(VI), are written as H_nMO_4 (V, H_3VO_4 ; Ge, H_4GeO_4 ; Mo, H_2MoO_4 ; W, H_2WO_4). In the acidic pH region, these species exist predominantly as neutral or protonated species, such as H_nMO_4 or $H_{n+1}MO_4^+$. Around the neutral pH region, oxo-acid species could exist as anionic species, $H_{n-m}MO_4^{m-}$. Therefore, oxo-acid species might be adsorbed on the resins by a combination between chelating mechanism, anion-exchange mechanism, and hydrogen bonding mechanism with chelating moieties and the residual amino groups of chitosan itself. The adsorption mechanism of oxo-acids on chitosan resins might be different from that of metals and lanthanoids.

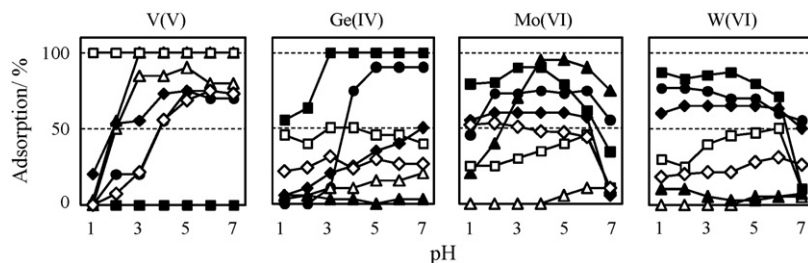


Fig. 4. Adsorption behavior of oxo-acids at pH 1–7 on chitosan resins. The experimental conditions and symbols are the same as in Fig. 2.

3.4. Adsorption behavior of uranium on chitosan resins

Fig. 5 shows the adsorption behavior of uranium on chitosan resins at pH 1–7. Chitosan resins could adsorb U(VI) effectively as follows: IDP-type chitosan, pH 1–7; serine-type chitosan and catechol-type chitosan (type 2), pH 2–7; phenylarsonic acid-type chitosan and catechol-type chitosan (type 1), pH 4–7. It was caused by the modification of cross-linked chitosan (base material) with chelating moieties, because the chitosan resins with chelating moiety absorb U(VI) more effectively than the cross-linked chitosan. And then, the IDP-type chitosan adsorbed U(VI) at wider pH regions, whereas uranium adsorbed on it could not be eluted even with nitric acid and hydrochloric acid ($1\text{--}6\text{ mol L}^{-1}$). On the other hand, uranium adsorbed on other types of chitosan resin was eluted with 1 mol L^{-1} nitric acid thoroughly. Adsorption mechanism of U(VI) on IDP-type chitosan might be different from that on the other chitosan resins. The metal ions and lanthanoids exist as a cationic species, such as M^{n+} , whereas uranium exists as different species over the pH range and it is increasingly hydrolyzed and forms oligomeric species with an increase of pH. Uranium exists predominantly as monomeric species, UO_2^{2+} and partially as $UO_2(OH)^+$

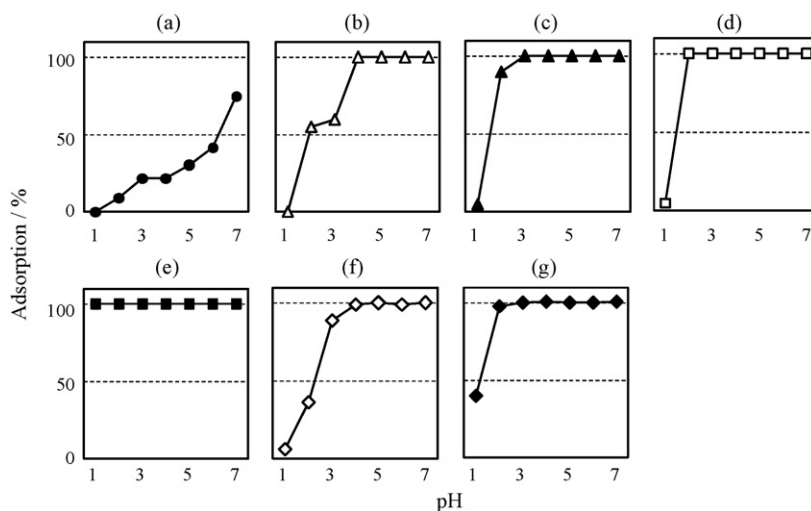


Fig. 5. Adsorption behavior of uranium at pH 1–7 on chitosan resins. Sample, 10 mL; concentration of each element, $10 \mu\text{g L}^{-1}$; column, 1 mL; eluent, 10 mL of 1 mol L^{-1} nitric acid. (a) Cross-linked chitosan; (b) catechol-type chitosan (type 1); (c) catechol-type chitosan (type 2); (d) IDA-type chitosan; (e) IDP-type chitosan; (f) phenylarsonic acid-type chitosan; (g) serine-type chitosan.

in acidic pH regions ($\text{pH} \leq 5$), and it forms colloidal or oligomeric species, such as $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_4(\text{OH})_7^+$, and $(\text{UO}_2)_3(\text{OH})_7^-$ around neutral pH regions ($\text{pH} \geq 5$). Therefore, the adsorption mechanism of U(VI) on chitosan resins is considered to be quite complicate. These chitosan resins might adsorb the species of UO_2^{2+} by forming the stable chelates with functional moieties introduced to the cross-linked chitosan. The serine-type chitosan and catechol-type chitosan (type 2) could adsorb U(VI) at wider pH regions ($\text{pH} 2\text{--}7$), which was readily eluted with 1 mol L^{-1} nitric acid, than the other chitosan resins. Also, compared chitosan resins with each other, the adsorption capacity of catechol-type chitosan (type 2, $0.14 \text{ mmol mL}^{-1}$) for Cu (II) was larger than that of serine-type chitosan ($0.08 \text{ mmol mL}^{-1}$). The catechol-type chitosan (type 2) might adsorb U(VI) at pH 2–7 by forming a stable chelate with hydroxyl groups of catechol moiety. Considering such adsorption ability and elution efficiency, catechol-type chitosan (type 2) was suitable for the selective and effective collection of uranium. The catechol-type chitosan (type 2) is expected to be applied to the on-line pretreatment prior to the uranium determination.

4. Conclusions

The adsorption behavior of trace elements, existing as cationic and anionic species in aquatic media, on chitosan resins was discussed in detail. Especially, catechol-type chitosan (type 2) could adsorb U(VI) at pH 2–7 by a chelating mechanism more effectively, and then the uranium collected on the resin was readily eluted. It might be effective material for the collection and concentration of trace uranium prior to the determination.

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