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Notes

Adsorption Properties of Ionic Species on Cross-linked Chitosans Modified with Catechol and Salicylic Acid Moieties

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Catechol-type chitosan resin and salicylic acid-type chitosan resin were easily synthesized for use in estimating the adsorption behavior of 34 elements at pH 1 – 7 in aquatic media. The catechol-type chitosan resin could adsorb Cu(II) at pH 3 – 7, In(III) at pH 4 – 6, Pb(II) and lanthanoids at pH 5 – 7, and U(VI) at pH 4 – 7 more effectively than the salicylic acid-type chitosan resin and the cross-linked chitosan resin (base material). Adsorption ability was in the order: catechol-type chitosan resin > salicylic acid-type chitosan resin > cross-linked chitosan resin.

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Introduction

Chitosan, which is a glucosamine biopolymer obtained by deacetylating chitin, is used as one of the useful base materials for the development of chelating resins and ion-exchange resins. Also, chitosan is of great interest due to the advantages, such as easy derivatization of its amino group, and more hydrophilic than the synthetic base materials like polystyrene-divinylbenzene copolymer, which provides fast sorption of ionic species in aquatic media.[1] Some researchers have applied chitosan to the collection of trace elements in water samples prior to trace analysis.[2-4] In order to develop high-performance chitosan resins for the pretreatment of water samples, many researchers have discussed the adsorption properties of cationic species, such as heavy metals and lanthanoids on chitosan resins modified with chelating moieties, such as iminodiacetic acid (IDA) group, ethylenediaminetetraacetic acid (EDTA) group, diethylenetriaminepentaacetic acid (DTPA) group, methylthiocarbamoyl group, phenylthiocarbamoyl group, 2-pyridylmethyl group, 2-thienylmethyl group, and 3-(methylthio)propyl group.[5-10] In order to elucidate the adsorption properties, we must systematically examine the adsorption behavior of several similar elements at various pH conditions. In our previous work, we developed some chitosan resins possessing amino acid as a chelating moiety for the preconcentration of trace elements in aquatic samples prior to the ICP-MS measurement.[11-13] Also, we elucidated the adsorption ability of chitosan resins possessing one amino acid moiety, such as glycine, leucine, valine, or serine, by using the proposed column procedure.[14]

In this study, cross-linked chitosan resins modified with salicylic acid and catechol were easily synthesized and the adsorption behavior of cationic and anionic species on the resins was systematically examined by using the column procedure. And then we discussed and elucidated the adsorption ability of chitosan resins for the collection and separation of cationic and anionic species in aquatic media.

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Experimental

Reagents and chemicals

The chitosan (Tokyo Kasei Co. Ltd., Tokyo, Japan) was in a flake form, whose deacetylated degree was about 80%. All other reagents used for the preparation of chitosan resins were of analytical reagent grade.

The stock solution of an analytical standard for elements was prepared by diluting several kinds of single-element standard solutions for atomic-absorption spectrometry (1000 μg ml^{-1}; Wako Pure Chemicals, Osaka, Japan) and a multi-element standard solution for ICP-MS provided by Spex CertiPrep Inc. (Metuchen, NJ, USA). This stock solution was diluted by weight just before each column procedure with 0.1 M nitric acid to give 10 ng ml^{-1} of each element.

Ultrapure-grade nitric acid (60%; density, 1.38 g ml^{-1}; Kanto Chemicals, Tokyo, Japan) was diluted with ultrapure water. Acetic acid (minimum 96%) and ammonia water (29%), which were of electronic industrial reagent grade purchased from Kanto Chemicals (Tokyo, Japan), were used for preparing the ammonium acetate solution. Ultrapure water (18.3 MΩ cm^{-1} resistivity), prepared by an Elix 3/Milli-Q Element system (Nihon Millipore, Tokyo, Japan), was used throughout.

Synthesis of chitosan resins

The chemical structures of the cross-linked chitosan resin (base material) and the cross-linked chitosan resins modified with catechol moiety (catechol-type chitosan resin) and with salicylic acid moiety (salicylic acid-type chitosan resin) are shown in Fig. 1.

The cross-linked chitosan resin was synthesized in a similar manner to that previously described.[15] Chitosan flakes (20 g), which were ground to fine pieces and sieved to obtain chitosan particles of diameter (100 – 300 μm), were suspended in ethanol

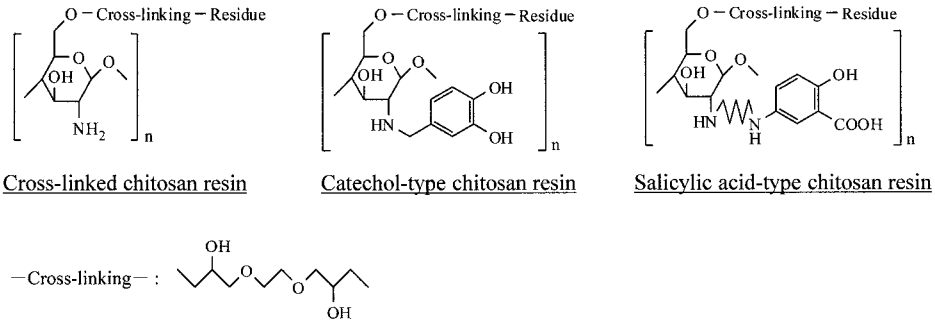

Fig. 1 Chemical structures of chitosan resins.

(200 ml). Benzaldehyde (80 g) was then added to the suspension. The mixture was stirred at room temperature for 12 h to protect the amino groups of chitosan as a Schiff base. After the reaction, the product was filtered and washed with ethanol and water to remove unreacted benzaldehyde. The chitosan derivative protected the amino groups with benzaldehyde, was refluxed with ethyleneglycoldiglycidylether (EGDE, 30 g) in dioxane (300 ml) and 1 M NaOH (40 ml) for 3 h. The product was filtered and washed with ethanol and water. The Schiff base was cleaved to an amino compound by twice stirring the product in 0.5 M HCl (1000 ml) at room temperature for 12 h, followed by filtration and washing with ethanol and water, respectively.

The catechol-type chitosan resin and the salicylic acid-type chitosan resin were newly synthesized through Schiff base formation between amino groups and aldehydes, and were reduced with sodium tetraborate. The catechol-type chitosan resin was prepared as follows. The cross-linked chitosan resin (5 g) was suspended in ethanol (200 ml), then 3,4-dihydroxybenzaldehyde (15 g) was added to the suspension, and the mixture was stirred at room temperature for 24 h. After the reaction, the product was filtered and washed 3 times with ethanol to remove any residual reagents. Secondly, the product and sodium tetrahydroborate (15 g) were suspended in ethanol (100 ml). The mixture was stirred for 6 h. The final product was filtered and washed 3 times with ethanol and 3 times with water. The salicylic acid-type chitosan resin was prepared as follows. First, the cross-linked chitosan resin (5 g) was suspended in ethanol (200 ml), then glutaraldehyde (40 g) was added to the suspension, and the mixture was stirred for 3 h. The product was filtered and washed 3 times with ethanol to remove any residual reagents. Secondly, the product and 5-aminosalicylic acid (15 g) were suspended in ethanol (200 ml), and the mixture was stirred for 24 h. After the reaction, the final product was filtered and washed 3 times with ethanol and 3 times with water. Thirdly, the product and sodium tetrahydroborate (15 g) were suspended in ethanol (100 ml), and the mixture was stirred for 6 h. After that, the final product was filtered and washed 3 times with ethanol and 3 times with water. The IR spectra of the catechol-type chitosan resin and salicylic acid-type chitosan resin, compared with that of the cross-linked chitosan resin as a base material, showed the additional bands at 811 and 817 cm^{-1}, respectively. These bands are due to the benzene rings of catechol moieties and salicylic acid moieties introduced into the cross-linked chitosan resin. These chitosan resins were used for the following column procedure.

Apparatus

The ICP-MS system used for measuring 34 elements was a Model SPQ 8000H (Seiko Instruments, Chiba, Japan). The operating conditions are summarized in Table 1. IR (infrared) spectra were taken by the KBr pellet method using an FT/IR-4100 spectrometer (JASCO Co., Tokyo, Japan).

Table 1 Operating conditions for ICP-MS instruments

Instrument	Seiko SPQ 8000H: Quadrupole type
Frequency/MHz	27
Incident power/kW	1.1
Reflected power/W	< 5
Plasma gas	Ar 15 l min^{-1}
Carrier gas	Ar 0.45 l min^{-1}
Auxiliary gas	Ar 1.0 l min^{-1}
Sampling depth	10 mm from load coil
Sampling cone	Copper 1.1 mm orifice diameter
Skimmer cone	Copper 0.35 mm orifice diameter

Column procedure

Before a column procedure, each chitosan resin was cleaned up to remove any residual metallic impurities in the resin as follows: 20 ml of wet resin was transferred to a 100-ml plastic beaker containing 80 ml of 2 M nitric acid; the mixture was carefully stirred at a low speed for 6 h. The resin was then filtered and rinsed with ultrapure water.

The column procedure was similar manner to that described in our previous work.[14] The resin (wet volume, 1 ml) was packed in small-sized polypropylene columns (mini-column: 1 ml of volume, 5.0 i.d. × 50 mm, Muromachi Chemical, Kyoto, Japan), which were used to examine the adsorption and recovery of 34 elements on the resin. For washing resin packed in a mini-column, each 10 ml of 1 M nitric acid and ultrapure water was passed through the column. Then, 5 ml of a conditioning solution (pH 1 – 2, 0.1 M and 0.01 M nitric acid; pH 3 – 7, 0.5 M ammonia–acetate solution) was passed through the column for pH conditioning of each column. A sample solution (10 ml), whose pH was adjusted with the conditioning solution, was passed through the column. Then, a 5-ml aliquot of a rinsing solution (pH 1 – 2, 0.1 M and 0.01 M nitric acid; pH 3 – 7, 0.2 M ammonia–acetate solution) was passed through each column to remove any matrices remaining on the resin. Then, a 5-ml portion of ultrapure water was passed through the column to rinse the remaining components of the rinsing solution. Finally, 10 ml potions of 1 M nitric acid were passed through the column to recover the elements adsorbed on the resin. The elements in these effluents were determined by ICP-MS. Throughout all the column procedures, the flow rate was maintained at about 1 ml min^{-1}.

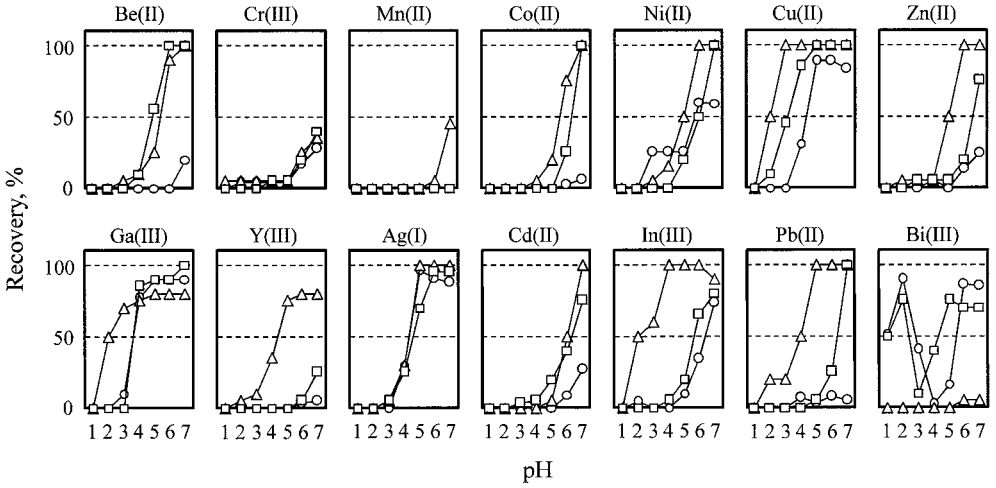

Fig. 2 Adsorption behavior of metals at pH 1 – 7 on chitosan resins. Sample, 10 ml; concentration of each element, 10 ng ml^{-1}; column, 1 ml; eluent, 10 ml of 1 M nitric acid. ○, Cross-linked chitosan resin; △, catechol-type chitosan resin; □, salicylic acid-type chitosan resin.

Results and Discussion

The adsorption capacities of Cu(II) on the catechol-type chitosan resin and on the salicylic acid-type chitosan resin were examined. In general, Cu(II) can form the stabler chelate with various chelating reagents than the other metal ions. The adsorption capacities of the catechol-type chitosan resin and the salicylic acid-type chitosan resin were 0.08 mmol ml^{-1} and 0.06 mmol ml^{-1}, respectively. These capacities were in large excess of the amount (10 ng ml^{-1}) of each element which was examined in following experiments.

The adsorption behavior of 34 elements on chitosan resins was examined by using the column procedure. Figure 2 shows the adsorption behavior of metal ions such as Be(II), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Y(III), Ag(I), Cd(II), In(III), Pb(II), and Bi(III), which can exist as cationic species in aquatic media. These cationic species adsorbed on the cross-linked chitosan resin (base material), catechol-type chitosan resin, and salicylic acid-type chitosan resin could be thoroughly eluted with 10 ml of 1 M nitric acid as an eluent. The catechol-type chitosan resin and the salicylic acid-type chitosan resin could adsorb such cationic species more effectively than the cross-linked chitosan resin. The catechol-type chitosan resin could adsorb Cu(II) at pH 3 – 7, In(III) at pH 4 – 6, Ag(I) and Pb(II) at pH 5 – 7, Zn(II) at pH 6 – 7, and Be(II), Co(II), and Cd(II) at only pH 7 quantitatively, whereas the salicylic acid-type chitosan resin could adsorb Cu(II) at pH 5 – 7, Be(II) and Ag(I) at pH 6 – 7, and Co(II), Ni(II), Ga(III), and Pb(II) at only pH 7. These cationic species might form chelates with the catechol and salicylic acid moieties introduced to the cross-linked chitosan resin as a base material. Especially, catechol-type chitosan resin could adsorb Cu(II), In(III), and Pb(II) at lower pH regions than the other chitosan resins, which is due to forming stable chelates between the catechol moiety in the resin. The adsorption behavior of Bi(III) is distinct from that of the other cationic species, whereas the adsorption behavior of Bi(III) on the salicylic acid-type chitosan resin is similar to that on the cross-linked chitosan resin, which might be due to forming its chelate with amino groups of chitosan itself. However, catechol-type chitosan resin could not adsorb it. The cathechol moiety, which can be directly introduced to the amino group of chitosan, might be a steric hindrance to the bismuth adsorption. Figure 3 shows the adsorption behavior of lanthanoids and actinoids on chitosan resins at pH from 1 to 7. Lanthanoids can exist as cationic species, Ln(III), in aqueous solution. The catechol-type chitosan resin could adsorb the lanthanoids at wider pH regions from 5 to 7 and could adsorb the actinoids, such as U(VI) and Th(IV), more effectively than the salicylic acid-type chitosan resin and the cross-linked chitosan resin. These cationic species, such as metals, lanthanoids, and actinoids, could form the chelates of five-membered rings with two hydroxyl groups (–OH) of catechol moiety in the resin and the chelates of six-membered rings with a hydroxyl group (–OH) and a carboxyl group (–COOH) of salicylic acid moiety. Therefore, the catechol-type chitosan resin might adsorb such cationic species at wider pH regions by forming stable chelate. The adsorption ability of such cationic species on examined chitosan resins at pH 1 – 7 is in the following order: catechol-type chitosan resin > salicylic acid-type chitosan resin > cross-linked chitosan resin, such an order is concerned with the complex formation constants between the cationic species and the chelating moieties introduced to the resin. These chitosan resins might adsorb the cationic species by forming chelates with the chelating moieties and the residual amino groups of the chitosan itself.

On the other hand, the adsorption behavior of oxo-acids, such as V(V), Ge(IV), Mo(VI), and W(VI), on chitosan resins is quite distinct from that of the cationic species described above. Figure 4 shows the adsorption behavior of oxo-acids on chitosan resins at pH 1 – 7. At the acidic pH regions, oxo-acids exist predominantly as neutral species or protonated species. Around the neutral pH regions, these exist as anionic species. Oxo-acids might be adsorbed by the combinations of anion-exchange mechanism, hydrogen bonding mechanism, and chelating mechanism with amino group, hydroxyl group, and carboxyl group in the chitosan and chelating moieties. The cross-linked chitosan resin and the salicylic acid-type chitosan resin adsorb such oxo-acids more effectively, whereas the catechol-type chitosan resin could not adsorb Ge(IV), Mo(VI), and W(VI). This result might be also due to the steric hindrance of catechol moiety bonded at the amino group of chitosan.

In conclusion, the adsorption behavior of 34 elements on chitosan resins was systematically examined by the column

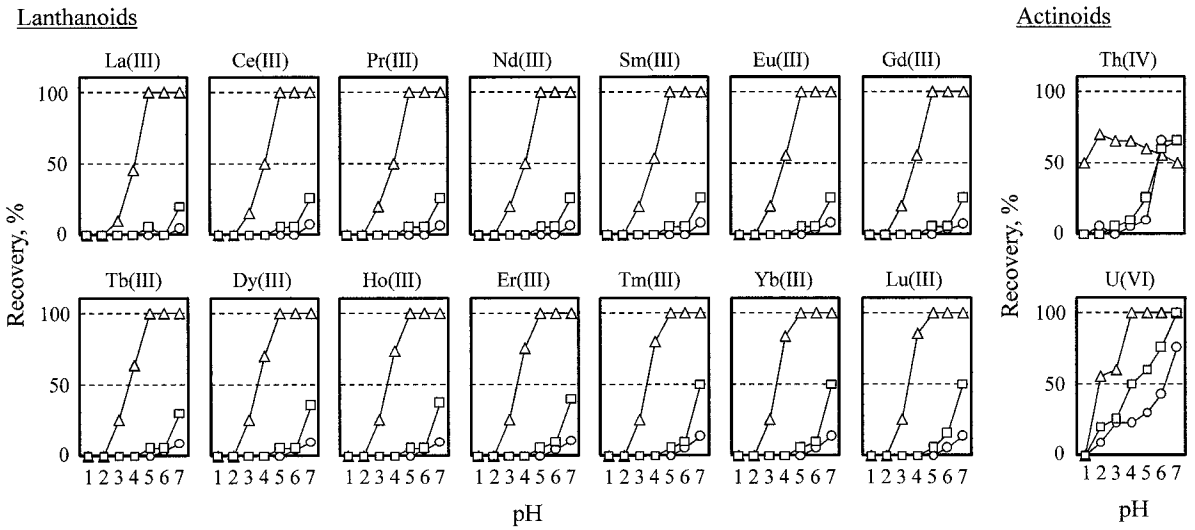

Fig. 3 Adsorption behavior of lanthanoids and actinoids at pH 1 – 7 on chitosan resins. The experimental conditions and symbols are the same as in Fig. 2.

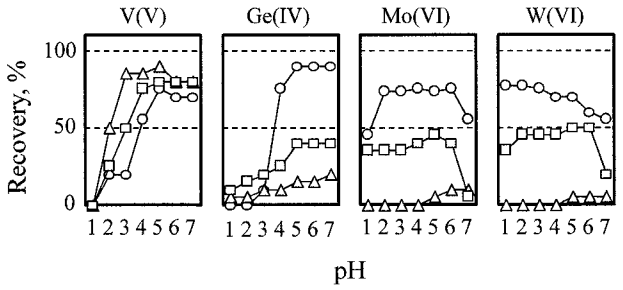

Fig. 4 Adsorption behavior of oxo-acids at pH 1 – 7 on chitosan resins. The experimental conditions and symbols are the same as in Fig. 2.

procedure. Cationic species, such as metals, lanthanoids, and actinoids, could be adsorbed by chelating mechanism, whereas oxo-acids, such as V(V), Ge(IV), Mo(VI), and W(VI), might be adsorbed on the resin by a combination of anion-exchange mechanism, hydrogen bonding mechanism, and chelating mechanism. The adsorption ability of cationic species on chitosan resins was in the order: catechol-type chitosan resin > salicylic acid-type chitosan resin > cross-linked chitosan resin.

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