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Adsorption Behavior of Mercury and Precious Metals on Cross-Linked Chitosan and the Removal of Ultratrace Amounts of Mercury in Concentrated Hydrochloric Acid by a Column Treatment with Cross-Linked Chitosan

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Cross-linked chitosan was synthesized with chitosan and ethylene glycol diglycidyl ether. The adsorption behavior of trace amounts of metal ions on the cross-linked chitosan was systematically examined by packing it in a mini-column, passing a metal solution through it and measuring metal ions in the effluent by ICP-MS. The cross-linked chitosan adsorbed mercury and precious metals (Pd, Pt, and Au) at pH values from acidic to neutral. Especially, mercury in concentrated hydrochloric acids could be adsorbed on cross-linked chitosan quantitatively by an anion-exchange mechanism in the form of a stable chloride complex. This method was applied to the removal of mercury from commercially available hydrochloric acid; more than 97% of mercury was removed, and the residual mercury in the hydrochloric acid (Grade: for trace analysis) was found to be 0.15 ppb. Mercury adsorbed on the cross-linked chitosan could be easily desorbed with an eluent containing 1 M hydrochloric acid and 0.05 M thiourea. The thus-refreshed cross-linked chitosan could be repeatedly used for the removal of mercury in hydrochloric acid.

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Introduction

Chitosan, an *N*-deacetylation product of chitin, is one of the useful chelating polymers. Muzzarelli and Tubertini reported that chitosan could adsorb transition-metal ions from aqueous solutions at neutral pH.[1,2] Chitosan could also adsorb Hg(II), Cu(II), Cr(III), Pb(II), UO_2^{2+} and Cd(II).[3-8] Chitosan, however, is found to be easily soluble in some acidic media, such as nitric acid, hydrochloric acid, and acetic acid. This is one of the serious disadvantages from a practical point of view for metal collection and concentration. In order to overcome the problem of high solubility in some acids, several types of chemically cross-linked chitosan have been synthesized, and their metal adsorption properties have already been examined. Cross-linking can make chitosan sparingly soluble in acidic media. Ohga *et al*.[9] prepared cross-linked chitosan with chloromethyloxyrane after the complexation of chitosan with metal ions; it could act as effective adsorbents for Cu(II) and Hg(II). Inoue *et al*. reported the adsorption behavior of 15 elements on cross-linked chitosan by a batchwise method.[10,11] Koyama *et al*. also synthesized cross-linked chitosan with glutaraldehyde, and examined the adsorption behavior of Cu(II).[12,13] Further, Rorrer *et al*. examined the adsorption isotherms of Cd(II) on porous chitosan beads, which were cross-linked with glutaraldehyde, at 25˚C and pH 6.5, over the concentration ranges from 1 – 1690 mg l^{-1}.[14] These studies examined mainly the adsorption behavior of several metal ions at ppm levels in a pH region from 4 to 7 on cross-linked chitosan by batchwise equilibration techniques, and did not aim at collecting and concentrating trace-to-ultratrace amounts of metal ions at ppb – sub-ppb levels (1 ppb = 1 ng ml^{-1}), and also at removing trace metals in concentrated acids.

In our previous work,[15] the adsorption behavior of 60 elements at the 10 ng ml^{-1} level by a column pretreatment method using commercially available highly porous cross-linked chitosan beads (CHITOPEARL AL-01, Fuji Spinning Co., Ltd., Tokyo, Japan) was examined in detail. A useful ability as a packing material for collecting and concentrating trace amounts of metal ions was found. Furthermore, CHITOPEARL AL-01 could be applied to the determination of six oxoanions in river-water samples. CHITOPEARL AL-01, however, exhibits shrinkage characteristics, resulting in complicated column pretreatment procedures. In previous work,[16] we synthesized a new type of cross-linked chitosan by cross-linking the 6-hydroxyl group of chitosan with ethylene glycol diglycidyl ether. The newly synthesized cross-linked chitosan did not shrink, and even dissolved in concentrated acids. This chitosan could adsorb some metal ions by two different mechanisms: for Cu(II) and Ag(I), it could adsorb by a chelating mechanism, whereas for anionic species existing as oxoanions, such as V, Ga, Mo, W, and Bi, and existing as chloro complexes, such as Hg, Pt, Pd, and Au, by an anion exchange mechanism. The adsorption behavior of mercury and some precious metals, however, was not examined in detail.

In this work, the adsorption behavior of mercury and such precious metals as Pd(II), Pt(IV), and Au(III) at the 10 ng ml^{-1} level on the cross-linked chitosan packed in a mini-column was systematically examined in detail. The method was applied to the removal of mercury existing as an impurity in commercially available concentrated hydrochloric acid.

Experimental

Instrumentation

The ICP-MS system used for the determination of elements was a Model SPQ 8000H (Seiko Instruments Co., Tokyo, Japan). The experimental conditions were the same as those reported in our previous work.[17]

Materials and reagents

Chitosan flake, the deacetylated degree of which was about 80%, was purchased from Tokyo Kasei Co., Ltd. (Tokyo, Japan). All other reagents used for the synthesis of cross-linked chitosan were of analytical reagent grade. Anionic exchange resins of a strongly basic type (Dowex, SBR-P 21K, 20 – 50 MESH, Cl FRM) and a weakly basic type (Dowex, WGR, 20 – 50 MESH, FREE FRM) were purchased from The Dow Chemical Company (Midland, USA).

A mixing standard stock solution containing Hg(II), Pd(II), Pt(IV) and Au(III) (each 10 μg ml^{-1}) was prepared by diluting single-element standard solutions for atomic-absorption spectrometry (1000 μg ml^{-1}, Wako Pure Chemicals, Osaka, Japan) with 0.1 M hydrochloric acid or 0.1 M nitric acid. This stock solution was diluted with 0.1 M hydrochloric or nitric acid to give 10 ng ml^{-1} of each metals just before a column pretreatment. Accurate dilution of the standard solutions was carried out by weight.

Ultrapure grade hydrochloric acid (30%, Kanto Chemicals, Tokyo, Japan) and ultrapure grade nitric acid (60%, density 1.38 g ml^{-1}, Kanto Chemicals, Tokyo, Japan) were used. Acetic acid (minimum 96%) and ammonia water (29%) were of electronic industrial reagent grade (Kanto Chemicals, Tokyo, Japan), and were used for preparing an ammonium acetate buffer solution. Hydrochloric acid and thiourea used for an eluent were of extrapure grade (Kanto Chemicals, Tokyo, Japan).

Ultrapure water (18.3 MΩ cm resistivity) prepared by a Milli-Q Element System (Nihon Millipore, Tokyo, Japan) was used throughout.

Synthesis of cross-linked chitosan

Cross-linked chitosan was synthesized in three steps in a similar manner to previous work.[16] After chitosan flakes were broken into smaller pieces, chitosan particles with a diameter of 100 – 300 μm were collected with a sieve. After amino groups of the chitosan were protected by benzaldehyde,[18] the hydroxyl groups at the 6-position of chitosan were cross-linked with ethylene glycol diglycidyl ether (EGDE). Deprotection of amino groups was carried out with hydrochloric acid. The product was then filtered, and sufficiently washed with ethanol and water. The structure of the synthesized cross-linked chitosan is shown in Fig. 1.

Procedures with a mini-column treatment

Before use, the synthesized cross-linked chitosan and commercially available anionic exchange resins (strongly basic and weakly basic type) were cleaned to remove any residual metal impurities; 20 ml of the wet resin was transferred to a 100 ml plastic beaker, mixed with 80 ml of 2 M nitric acid, cautiously stirred at low speed for 6 h, and rinsed with ultrapure water. To the resins, after 80 ml of 1 M hydrochloric acid containing 0.05 M thiourea was added and stirred slowly for 6 h, the resins were rinsed with ultrapure water. The pretreated resins were packed in small-sized polypropylene columns (1 ml of volume, 5.0 – 5.5 mm i.d. × 50 mm, Muromachi Chemical, Kyoto, Japan) and used for the adsorption/concentration of metals in samples. An anion-exchange resin column was used for adsorption tests of anionic chloro complexes.

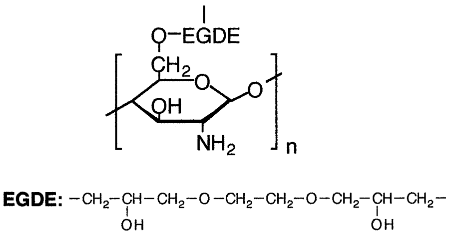

Fig. 1 Structure of synthesized cross-linked chitosan. Cited from Ref. 16.

The resin columns were washed and conditioned in a similar manner to our previous study.[15] One milliliter of the packed resin was washed with 10 ml of 1 M hydrochloric acid containing 0.05 M thiourea, 10 ml of 2 M nitric acid and then 10 ml of ultrapure water. Then, 10 ml of a buffer solution (pH 1 – 2: hydrochloric acid or nitric acid; pH > 3: 0.5 M acetate–ammonium buffer) was passed through the column for conditioning. Sample solutions (10 ml), the pHs of which were adjusted to the same values as the buffer for column conditioning, were passed through the column. Then, 10 ml of ultrapure water was passed for rinsing. Finally, 10 ml of the eluent containing 1 M hydrochloric acid and 0.05 M thiourea was passed through the column. The amount of metal ions in each effluent of the sample solution, ultrapure water and the eluent was determined by ICP-MS.

Throughout all of the column procedures, the flow rates were maintained at about 0.5 ml min^{-1}. The time required for a column pretreatment was about 2 h.

Procedure for removing mercury in concentrated hydrochloric acid

Small-sized polypropylene columns (1 or 10 ml of the volume; 5.0 – 5.5 mm i.d. × 50 mm or 10 – 11 mm i.d. × 118 mm, respectively; Muromachi Chemical, Kyoto, Japan), were used for pretreating cross-linked chitosan columns and anionic exchange resin columns.

One or five milliliters of the resins packed in a mini-column were washed with 20 ml of 1 M hydrochloric acid containing 0.05 M thiourea, 20 ml of 2 M nitric acid and then 20 ml of water. Forty milliliters of a concentrated hydrochloric acid as a sample were passed through the column; the first 20 ml of the effluent was discarded, and the second 20 ml of the effluent was used for the determination as residual mercury in hydrochloric acid by ICP-MS after diluting with ultrapure water.

Results and Discussion

Adsorption behavior of mercury and several precious metals on cross-linked chitosan and anionic exchange resins

Most of metal ions adsorbed on the cross-linked chitosan, except for Hg(II) and several precious metals, were completely eluted with 10 ml of 1 M nitric acid. For the effective elution of Hg(II) and several precious metals, 1 M hydrochloric acid containing 0.05 M thiourea was necessary, as reported in our previous papers.[15,16] This is because Hg(II) and precious metals can form stable complexes with thiourea.[15,19] Figure 2 shows the recovery of Hg(II) and several precious metals eluted from the synthesized cross-linked chitosan with 1 M hydrochloric acid containing 0.05 M thiourea. Among these metals, Hg(II)

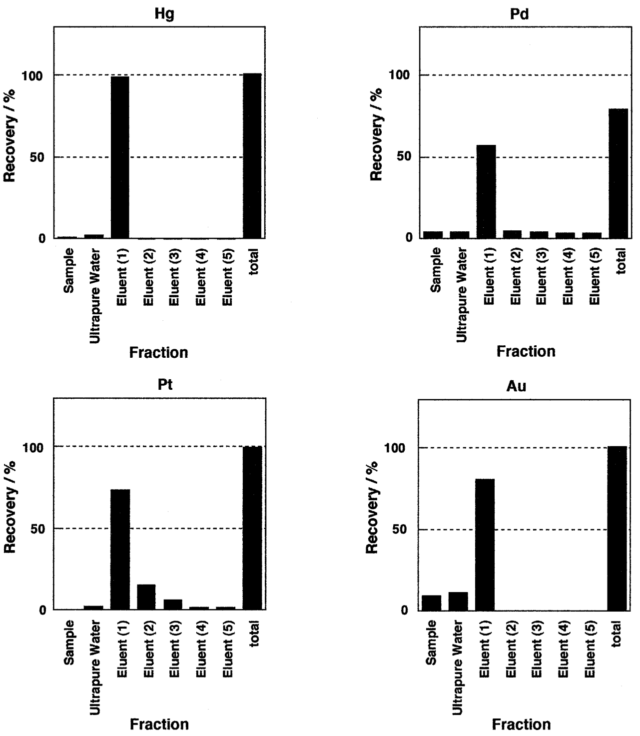

Fig. 2 Recovery of Hg, Pd, Pt, and Au adsorbed on cross-linked chitosan eluted with 1 M hydrochloric acid containing 0.05 M thiourea. Sample volume, 10 ml; concentration of each metal ion in sample solution, 10 ng ml^{-1}; ultrapure water for rinsing, 10 ml; volume of each eluent, 10 ml of 1 M hydrochloric acid containing 0.05 M thiourea; the figure in the parenthesis means the fraction number of the eluent; total value means the sum of the metals recovered in the throughout sample, ultrapure water and five replicated of the eluent.

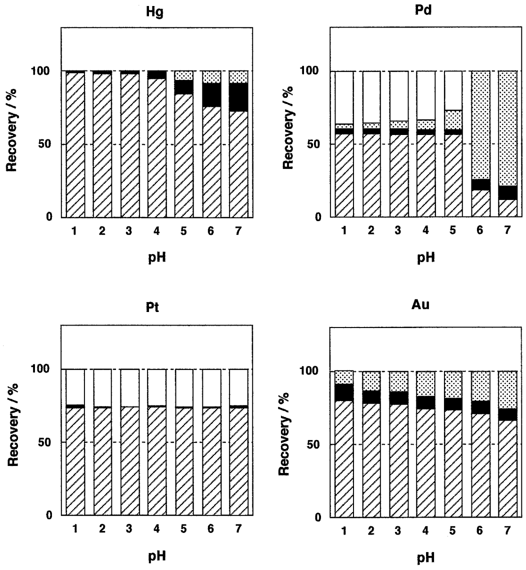

Fig. 3 Adsorption and elution behavior of trace elements, Hg, Pd, Pt, and Au at various pHs with cross-linked chitosan. Sample volume, 10 ml; concentration of each metal ions in the sample solution, 10 ng ml^{-1}; ultrapure water for rinsing, 10 ml; eluent, 10 ml of 1 M hydrochloric containing 0.05 M thiourea. ☐, no recovery; ▒, recovery in the recovered sample; ■, recovery in the recovered ultrapure water; ▨, recovery in the eluent (10 ml).

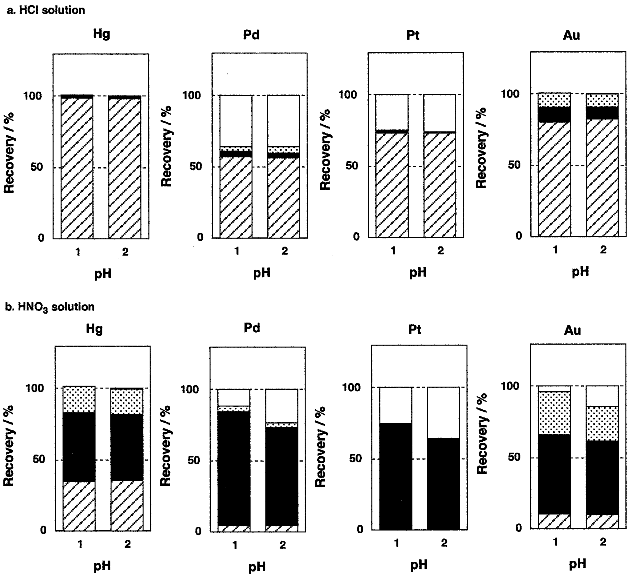

Fig. 4 Effect of chloride ion on the adsorption on the cross-linked chitosan. a. The sample solution was prepared with 0.1 M (pH 1) and 0.01 M (pH 2) hydrochloric acid. b. The sample solution was prepared with 0.1 M (pH 1) and 0.01 M (pH 2) nitric acid. The experimental conditions were the same as in Fig. 3.

was completely adsorbed and eluted; on the contrary, Pd(II), Pt(IV) and Au(III) could be adsorbed on the resin by 93%, 98% and 80%, respectively. Also, Au could be completely eluted with 10 ml of the eluent. The total of the recovered mercury as well as Pt and Au was almost 100%.

Figure 3 shows the effect of the pH on the adsorption behavior of Hg(II) and precious metals (Pd(II), Pt(IV), and Au(III)) from pH 1 to 7 with 10 ml of the eluent. The cross-linked chitosan could adsorb Hg(II) and precious metals over a wide pH region; these metals tended to be adsorbed on the cross-linked chitosan by an ion-exchange mechanism to the amino group of the chitosan. Some parts of Pd(II) and Pt(II) were difficult to be recovered with 10 ml of the eluent. Probably, various factors, such as ion exchange, chelating reaction and intercalation, seem to be intertwined in the strong adsorption of such metals. Figure 4 shows the effect of chloride ion on the adsorption of metals on cross-linked chitosan. Hydrochloric acid (0.1 and 0.01 M) or nitric acid (0.1 and 0.01 M) was used for preparing solutions of Hg(II) and precious metals, and conditioning the column. Hg(II) and precious metals readily formed chloro complexes when sample solutions were prepared with hydrochloric acid; therefore, anionic chloride complexes of these metals could adsorb on cross-linked chitosan by an anion exchange mechanism. On the contrary, when the sample solutions were prepared with nitric acid, Hg(II) could adsorb unsufficiently on the cross-linked chitosan. Because the commercially available standard solution of mercury was prepared with hydrochloric acid, and a small amount of chloride ion existed in the last sample solutions for the measurement.

To compare with the adsorption behavior of Hg(II) and precious metals on cross-linked chitosan, strongly and weakly basic-type anionic exchange resins were tested from pH 1 to 7. The results are shown in Figs. 5 and 6. The adsorption and elution of these metals with both anionic exchange resins were inferior; even Hg could not be recovered by less than 50% over the pH region examined. In general, chloro complexes of

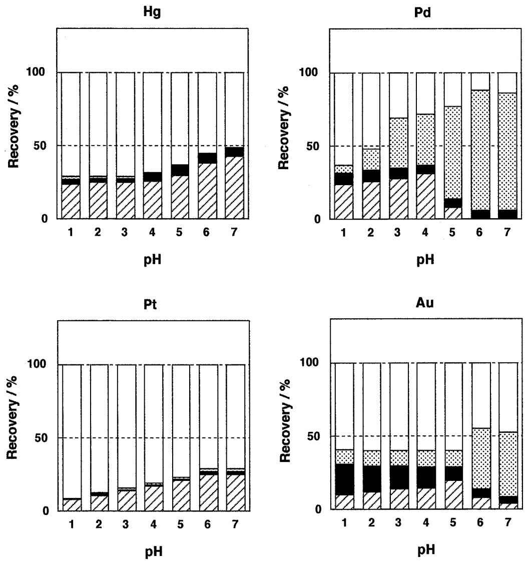

Fig. 5 Adsorption behavior of trace elements, Hg, Pd, Pt, and Au at various pHs with the strongly basic type anionic exchange resin. The experimental conditions were the same as in Fig. 3.

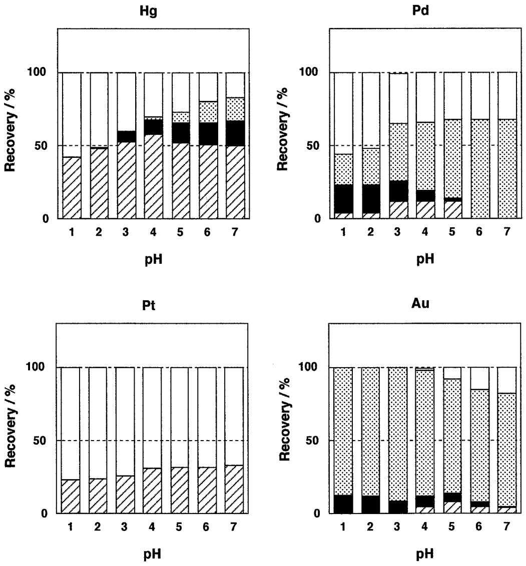

Fig. 6 Adsorption behavior of trace elements, Hg, Pd, Pt, and Au at various pHs with the weakly basic type anionic exchange resin. The experimental conditions were the same as in Fig. 3.

Hg(II) and precious metals can adsorb strongly on an anionic-exchange resin. In order to recover these metals, the resins adsorbing metals must usually be incinerated. In the case of using cross-linked chitosan, it is very easy to desorb these metals. At the point of elution with thiourea from the ion exchanger, the hydrophilic cross-linked chitosan resin having hydroxyl groups is superior to hydrophobic ion exchange resins made of polystyrene-divinylbenzene (PS-DVB).

Removal of trace and ultratrace amounts of mercury in concentrated hydrochloric acid

For the ultratrace analysis of mercury, the commercially available hydrochloric acid used was treated with cross-linked chitosan to remove any mercury existing as an impurity. The direct determination of mercury in hydrochloric acids by using a calibration graph is very difficult, since a high concentration (~11 M) of chloride interferes with the measurement by ICP/MS, and mercury in diluted HCl can not be determined for contents that are too low. By using hydrochloric acid purified with the chitosan column, 1 M HCl solutions spiked with various known amounts of mercury were prepared for a calibration graph, and determined in commercially available concentrated hydrochloric acids with no treatment. The obtained results are shown in Fig. 7. The calibration graph using purified hydrochloric acid passes through the origin, and the slope is in good agreement with that obtained using unpurified hydrochloric acid. The concentrations of mercury in the obtained concentrated hydrochloric acids are given in Table 1. Although the removal of mercury in concentrated hydrochloric acids was insufficient (about 75%) with 1 ml of cross-linked chitosan, most of the mercury in concentrated hydrochloric acids could be removed with 5 ml of cross-linked chitosan. The concentration of mercury in extrapure as well as the other lower grade hydrochloric acid purified with cross-linked chitosan was less than that of ultrapure hydrochloric acid.

Conclusion

The adsorption behavior of mercury and Pd, Pt, and Au on cross-linked chitosan was systematically investigated. The main advantages of cross-linked chitosan are summarized as follows: (1) cross-linked chitosan can adsorb ultratrace amounts of mercury at a low pH region, (2) it can be refreshed by washing with 1 M hydrochloric acid containing 0.05 M thiourea, and (3) it can remove mercury contained in commercially available concentrated hydrochloric acids by a simple procedure.

Acknowledgements

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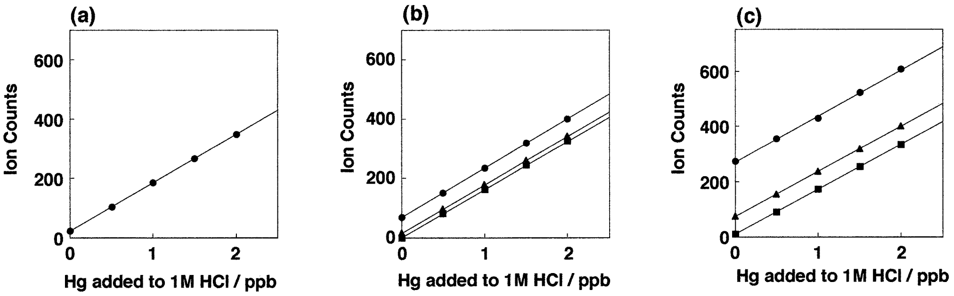

Fig. 7 Standard addition method for the mercury determination in concentrated hydrochloric acid. a, ultrapure grade; b, grade for trace analysis; c, extrapure grade. ●, without pretreatent; ▲, pretreatment with 1 ml of cross-linked chitosan; ■, pretreatment with 5 ml of cross-linked chitosan.

Table 1 Concentration and removal ratio of mercury in concentrated hydrochloric acid

Grade of conc. HCl	Concentration of Hg, ppb (removal ratio, %)		
	Without treatment	Pretreatment, resin volume	
		1 ml	5 ml
Ultrapure	1.31	—	—
For trace analysis	4.80	1.18 (75.4%)	0.15 (96.9%)
Extrapure	18.8	5.20 (72.2%)	0.79 (95.8%)

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