© 1997 The Chemical Society of Japan

Bull. Chem. Soc. Jpn., **70**, 2443—2447 (1997)

Adsorption of Lead(II) Ion on Complexane Types of Chemically Modified Chitosan

Katsutoshi Inoue,* Keisuke Ohto, Kazuharu Yoshizuka, Tomoo Yamaguchi, and Takeshi Tanaka

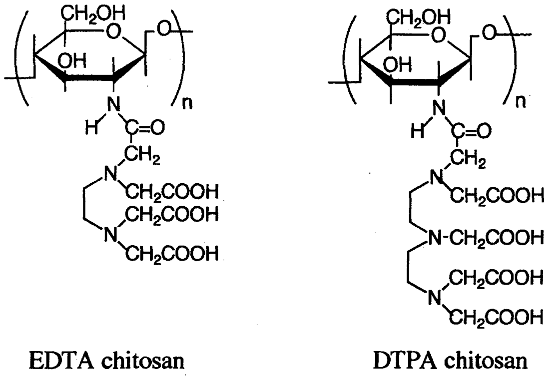
Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, 1-Honjo, Saga 840

(Received March 21, 1997)

Two kinds of complexane-type of chitosan chemically modified with EDTA and DTPA were synthesized and examined concerning the adsorption behavior for iron(III), copper(II), nickel(II), zinc(II), aluminium(III), and lead(II) from a dilute hydrochloric acid solution. Both of these adsorbents were found to adsorb lead(II) at low pH in a similar highly selective manner over zinc regardless of the kind of acid, whether it be hydrochloric acid or nitric acid, and to have a much stronger adsorption power compared with a commercial phosphonamidic acid-type chelating resin. The maximum adsorption capacities of lead were 1.8 and 1.5 mol/kg-dry gel for DTPA- and EDTA-chitosan. The breakthrough followed by elution tests demonstrated that it is achievable to concentrate a small amount of lead(II) which has been very selectively separated from a large excess of zinc by using an adsorption column packed with these adsorbents.

Needless to say, lead is one of the typical toxic heavy metals. The environmental regulation concerning lead has become as much as 10-times more severe in recent years in Japan, and is forecasted to be more even severely strengthened in the future. People are anxious that lead in the environment, for example that in water leaked from landfill sites made of industrial wastes and ashes produced by municipal incineration plants, will be unable to be effectively removed, thus resulting in severe regulation, such as using conventional commercial adsorbents. Consequently, it is strongly desired that much more effectively and strong adsorbents for lead will be commercialized. Although some polyether carboxylic acid types of new chelating resins[1,2] or ionophores[3] and a solvent-extraction reagent with a macrocyclic structure[4] have been developed for the separation and removal of lead in recent years, it is desired that more effective adsorbents which can be manufactured in a simple manner at cheap production costs will be developed.

Recently, the authors developed some novel adsorbents based on chitosan for metal ions: crosslinked copper(II)-complexed chitosan[5] and some complexane types of chemically modified chitosan.[6,7] It was found that these adsorbents exhibit excellent adsorption behaviors for metal ions with high selectivity that is much superior to commercial chelating resins. The complexane types of chemically modified chitosan, those modified with functional groups of ethylenediamine–*N*,*N*,*N*′,*N*′-tetraacetic acid or diethylenetriaminepentaacetic acid, as shown in Scheme 1 (abbreviated as EDTA- and DTPA-chitosan, respectively, hereafter) particularly exhibited interesting adsorption behaviors for base metals and rare earths. That is, for example, it was found that they have abilities for mutual separation among adjacent rare earths, similar to the original chelating properties of EDTA and DTPA, very different from conventional chelating resins which have no ability for mutually separating rare earths. These results appear to suggest that the excellent chelating characteristics of EDTA and DTPA are still maintained after immobilizing these ligands on polymer matrices of chitosan.

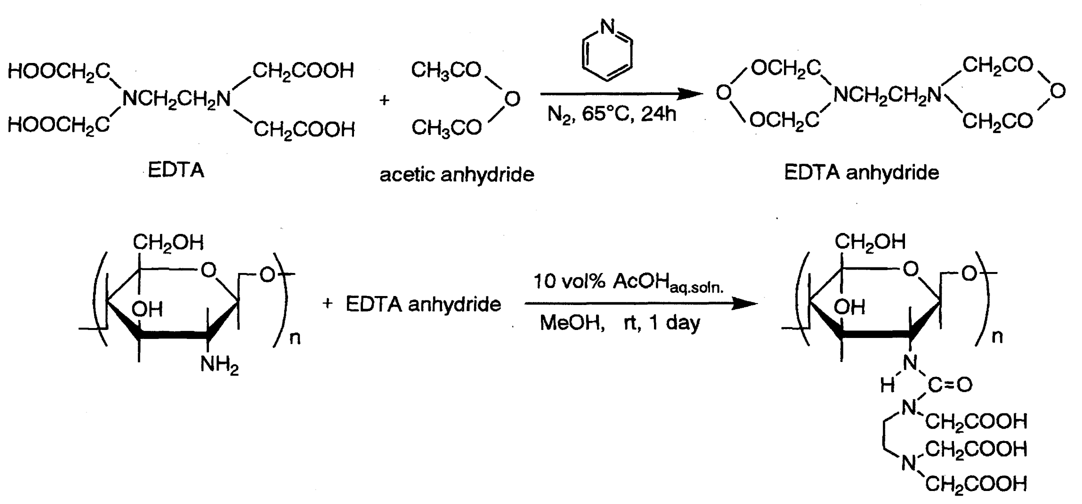


Scheme 1. Chemical structures of EDTA- and DTPA chitosan.

In the present work, we investigated the adsorption behaviors of EDTA- and DTPA-chitosan for lead(II) ion, since they are expected to have high selectivity, owing to the high chelating stability of EDTA and DTPA with lead(II).

Experimental

Preparation of EDTA- and DTPA-Chitosan. The sample of chitosan, the extent of deacetylation of which was about 95%, was kindly donated by Katokichi Co., Ltd., Kan-onji, Japan. EDTA- and DTPA-chitosan were prepared in the same manner as described in previous papers[6,7] by interacting EDTA or DTPA anhydride suspended in methanol with chitosan dissolved in an aqueous acetic acid solution and diluted with methanol according to the reaction shown in Scheme 2 for EDTA-chitosan, as an example. The extent of introducing the functional groups of EDTA and DTPA, determined by neutralization titration, was about 100% and 30%, respectively. The low extent of introducing the DTPA functional group may be attributable to a steric hindrance by bulky functional groups or crosslinking between the polymer chains of chitosan by



Scheme 2. Synthetic route of EDTA-chitosan.

the functional groups.

Preparation of an Aqueous Solution of Metals. In experiments concerning the batchwise adsorption of a single kind of metal ion, aqueous solutions of various metal ions were prepared by dissolving reagent-grade metal chlorides or nitrates into a dilute hydrochloric or nitric acid solution to a required concentration. The initial metal concentration was about 1 mM, except for experiments aimed at examining the effect of the metal concentration. In breakthrough tests of lead(II) and zinc(II) from an adsorption column, an aqueous feed solution was prepared by dissolving a small amount of lead(II) nitrate into a dilute hydrochloric acid solution containing a large amount of zinc(II). The pH and metal contents in the feed solutions are mentioned in the figure captions of Figs. 7 and 8.

Adsorption Equilibria. In experimental runs where the effects of the hydrogen-ion concentration on the adsorption of various metal ions (Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+}, and Pb^{2+}) were examined, a weighed amount (about 20 mg) of the adsorbent gel dried in vacuo was mixed and shaken together with 15 cm^3 of a dilute hydrochloric acid or nitric acid solution containing a single kind of metal ion in a flask at 303 K for more than 24 h, which was confirmed to be long enough to attain equilibrium in a preliminary experiment. Experimental runs in which the effects of the initial metal concentration on the adsorption of lead were examined were also carried out in a similar manner under the condition of a constant initial hydrogen-ion concentration (= 10 mM) and varying lead concentration (1—100 mM). Concentrations of hydrogen ion and metal ions in the aqueous solutions before and after adsorption were measured by means of neutralization titration or a pH meter, and spectrophotometry using a Seiko model SAS 7500 atomic-absorption spectrophotometer, respectively. The amounts of adsorbed metal ions were calculated based on the metal concentrations before and after adsorption and the weight of dry gel. The distribution ratio was calculated as the ratio of the amounts of adsorbed metal ions to the metal concentration in the aqueous solution after adsorption.

Breakthrough and Elution Tests Using a Packed Column. The tests were carried out by using the adsorption column shown in Fig. 1 made of glass. The temperature was maintained at 303 K by a water jacket. The gel (0.4 g dry weight) was packed in an adsorption column mixed together with 26.2 g glass beads (avarage diameter = about 1.3 mm) in order to suppress any volume change due to swelling accompanied by a pH change after being soaked in an aqueous solution having a pH less than 3. In a breakthrough test, the feed solution was fed at flow rates of 8.1 and 7.9 $cm^3\,h^{-1}$ in the cases of EDTA- and DTPA-type chitosan, respectively, upward from the bottom of the column. The elution was carried out by feeding a 2.4 M hydrochloric acid solution at the same flow rate in the same direction after the breakthrough test ($1\ M = 1\ mol\,dm^{-3}$), followed by washing the gel by ion-exchanged water in order to remove any metal ion remaining in the column unadsorbed on the gel. The sample solutions from the outlet were collected by using a fraction collector, and the metal concentrations were measured using an atomic-absorption spectrophotometer.

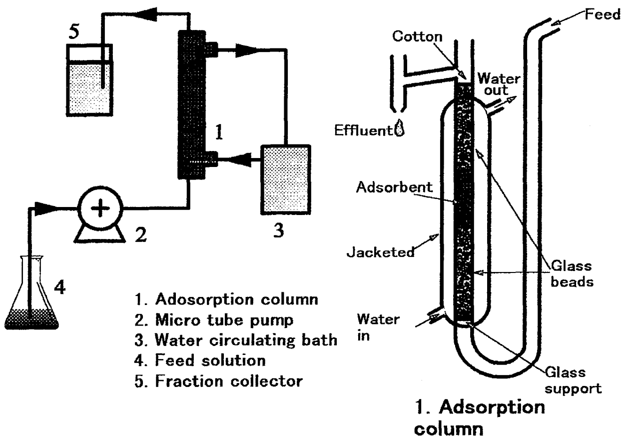


Fig. 1. Apparatus for column operation.

Results and Discussion

Effect of the Hydrogen-Ion Concentration on the Adsorption of Lead(II). Figures 2 and 3 illustrate the effects of the hydrogen-ion concentration on the distribution ratio of iron(III), copper(II), nickel(II), zinc(II), aluminium(III), and lead(II) in the adsorption on EDTA- and DTPA-chitosan, respectively, from a dilute hydrochloric acid solution. For both adsorbents, the sequence of the selectivity seriese of metal ions was nearly the same, as follows: Cu(II)≈Fe(III) > Ni(II) > Pb(II) > Zn(II) > Al(III). This sequence is also the same as that observed in the adsorption on these adsorbents from a dilute sulfuric acid solution[6,7] and in accordance with that of the stability constants of these metal ions with EDTA and DTPA. This means that the chelating characteristics

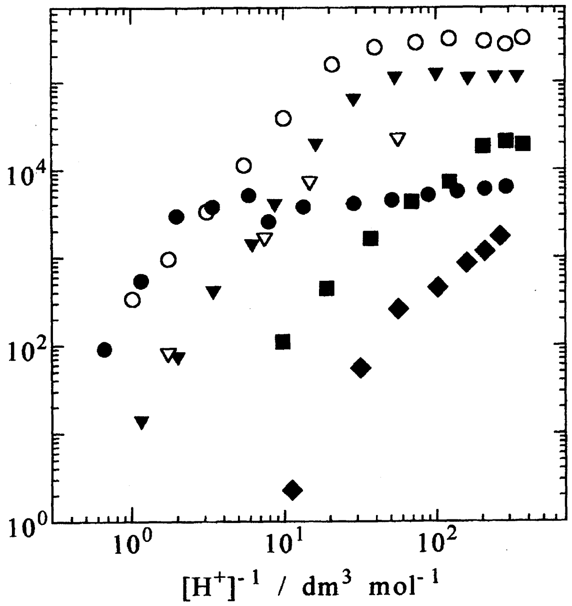


Fig. 2. Plots of the distribution ratio of iron(III), copper(II), nickel(II), zinc(II), aluminium(III), and lead(II) against equilibrium pH in the adsorption on EDTA-chitosan from dilute hydrochloric acid solution. ●: Fe^{3+}, ○: Cu^{2+}, ▼: Ni^{2+}, ■: Zn^{2+}, ◆: Al^{3+}, ▽: Pb^{2+}.

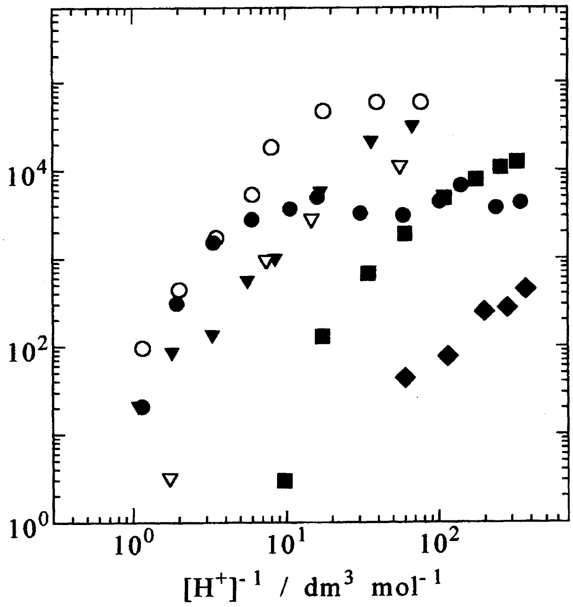


Fig. 3. Plots of the distribution ratio of iron(III), copper(II), nickel(II), zinc(II), aluminium(III), and lead(II) against equilibrium pH in the adsorption on DTPA-chitosan from dilute hydrochloric acid solution.●: Fe^{3+}, ○: Cu^{2+}, ▼: Ni^{2+}, ■: Zn^{2+}, ◆: Al^{3+}, ▽: Pb^{2+}.

of these ligands were still maintained after immobilization on polymer matrices of chitosan, as mentioned earlier. In both figures, the distribution ratio increases with decreasing hydrogen-ion concentration, and the plots tend to approach constant values corresponding to each metal ion, as observed in the adsorption on the usual chelating resins and solvent extraction. However, the plots for DTPA-chitosan tend to approach constant values at a lower distribution ratio compared with those for EDTA-chitosan. In both figures, high selectivity to lead over zinc is remarkable and interesting from a practical point of view, since lead always occurs together with zinc in nature owing to their chemical similarity.

Figure 4 shows a comparison of the adsorption of lead(II) ion between on EDTA- and DTPA-chitosan and between hydrochloric and nitric acids. As can be seen from this figure, all of the plots appear to cluster on nearly the same curve regardless of the kinds of acids, or those of ligands immobilized on chitosan.

Figure 5 shows a comparison of the adsorption of lead(II) ion between on EDTA- or DTPA-chitosan and on commercial phosphonamidic acid-type chelating resin (Sumichelate MC-95) from a hydrochloric acid solution. It is apparent that the adsorption takes place on EDTA- and DTPA-chitosan at a much lower pH than on MC-95 resin, suggesting that the complexane types of chemically modified chitosan can uptake lead(II) ion much more strongly than can commercial phosphonamidic acid-type chelating resin.

Adsorption Isotherm of Lead(II). Figure 6 illustrates the adsorption isotherms of lead(II) ion on both adsorbents, where the initial pH of the aqueous solution was kept constant at 2. The plots appear to lie on the Langmuir-type adsorption isotherms for both adsorbents, and tend to approach constant values of 1.8 and 1.5 mol/kg-dry gel for DTPA- and EDTA-type chitosan, respectively, the maximum adsorption capacities.

Breakthrough and Elution Tests. In order to demonstrate the separation and concentration of a small amount of lead(II) coexisting in a large excess amount of zinc(II)

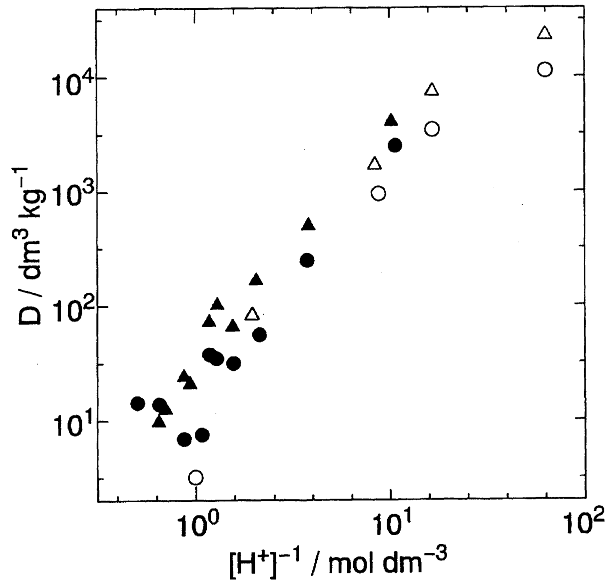


Fig. 4. Comparison of the adsorption of lead(II) between EDTA- and DTPA-chitosan, and between dilute hydrochloric and nitric acid solutions. ○: adsorption on DTPA-chitosan from HCl solution, △: adsorption on EDTA-chitosan from HCl solution, ●: adsorption on DTPA-chitosan from HNO_3 solution, ▲: adsorption on EDTA-chitosan from HNO_3 solution.

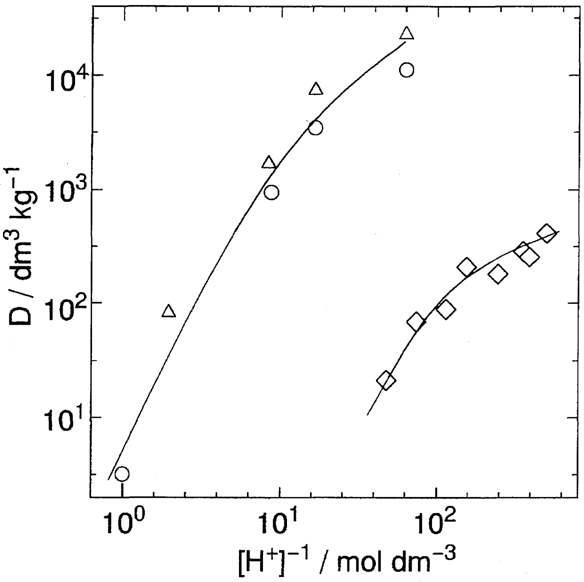


Fig. 5. Comparison of the adsorption of lead(II) between the complexane types of chemically modified chitosan and commercial phosphonamidic acid type of chelating resin. ○: DTPA-chitosan, △: EDTA-chitosan, ◇: MC-95 resin.

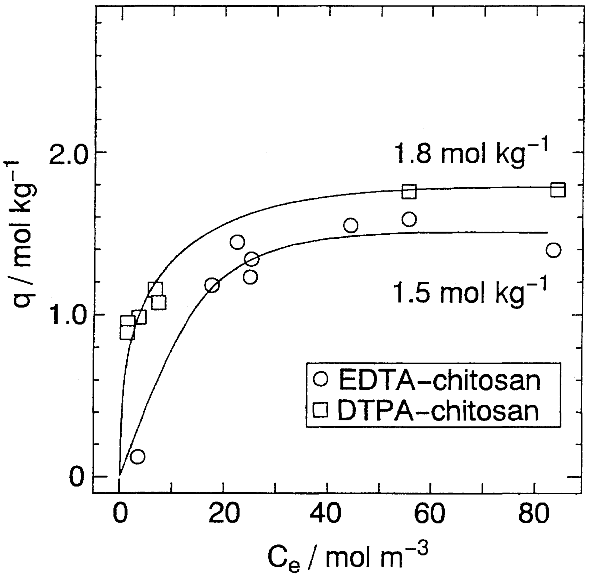


Fig. 6. Adsorption isotherms of lead(II) from hydrochloric acid solution at pH≈2 on EDTA- and DTPA-type chitosan.

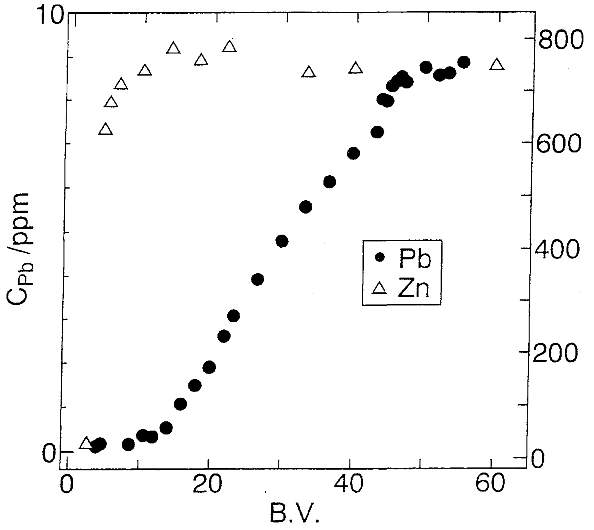


Fig. 7. Breakthrough profiles of lead(II) and zinc(II) in dilute hydrochloric acid solution from the column packed with EDTA-chitosan. Feed solution: pH = 1.06, metal contents = 10 ppm for lead and = 730 ppm for zinc. Flow rate of the feed solution: 8.1 ml h^{-1}.

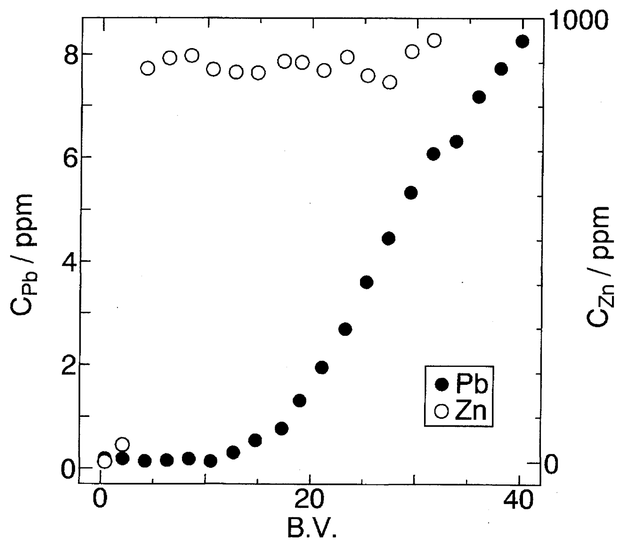


Fig. 8. Breakthrough profiles of lead(II) and zinc(II) in dilute hydrochloric acid solution from the column packed with DTPA-chitosan. Feed solution: pH = 1.78, metal contents = 10 ppm for lead and = 900 ppm for zinc. Flow rate of the feed solution: 7.9 ml h^{-1}.

in aqueous solutions by the present adsorbents, the breakthrough test, followed by elution test, was carried out using an adsorption column packed with EDTA- or DTPA-type chitosan. Figures 7 and 8 illustrate the breakthrough profiles of lead and zinc from columns packed with EDTA- and DTPA-type chitosan, respectively, under the condition mentioned earlier or in the figure captions. The abscissa in these figures (B.V.) refers to the dimensionless effluent volume, which is defined as the volume ratio of the effluent to the volume of the adsorption bed. The breakthrough of lead begins at about 10 B.V., while that of zinc begins immediately just after the initiation of the feed for both adsorbents, suggesting that an efficient and clear-cut separation between two metal ions can be achieved by using these adsorbents, as expected from the batchwise experimental results shown in Figs. 2 and 3. Figure 9 shows the elution profile of lead(II) and zinc(II) from a loaded column packed with EDTA-type chitosan by a 2.4 M hydrochloric acid solution as a typical example. A very sharp elution profile is observed at about 3 B.V. for lead concentrated as high as more than 40 times compared with the feed solution, while the elution of zinc is a very small quantity compared with that of lead. A similar profile was also observed for elution from a loaded column packed with DTPA-type chitosan. These results demonstrate

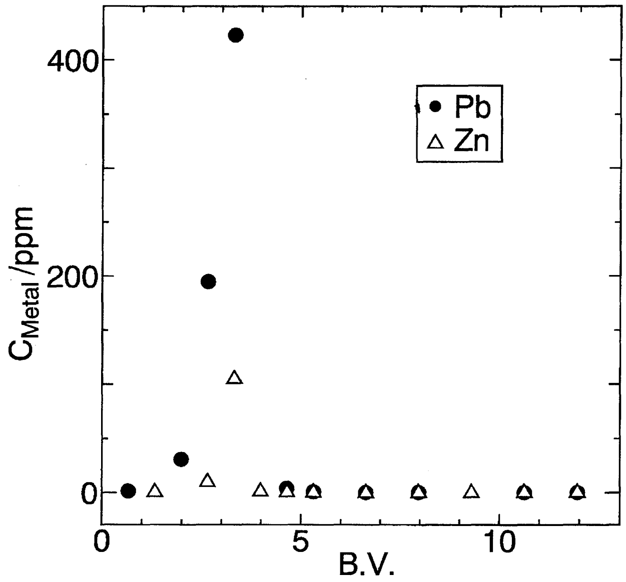


Fig. 9. Elution profiles of lead(II) and zinc(II) from the column packed with EDTA-chitosan with 2.4 M hydrochloric acid solution. Feed rate = 8.1 ml h^{-1}.

that the EDTA- and DTPA-chitosan developed in the present work have a high affinity and recognition ability for lead, suggesting that it is promissing to achieve a selective and effective removal of a small amount of lead in environment by using these adsorbents.

This work was financially supported in a part by the Salt Science Research Foundation (No. 9512).

References

1) T. Hayashita, K. Yamasaki, X. Huang, and R. A. Bartsch, *Chem. Lett.*, **1993**, 1487.

2) T. Hayashita, K. Yamasaki, K. Kunogi, K. Hiratani, X. Huang, Y. Yang, D. E. McGowen, and R. A. Bartsch, *Supramol. Chem.*, **6**, 347 (1996).

3) K. Hiratani, H. Sugihara, and K. Kasuga, Japanese Patent (Kokai), HEI 7-60080 (1995).

4) M. J. Gula, E. P. Horwitz, and D. B. Dreisinger, in "Zinc and Lead '95, Proc. Int. Symp. Extr. Appl. Zinc and Lead," ed by T. Azakami, MMIJ, Tokyo (1995), pp. 310—317.

5) K. Inoue, Y. Baba, and K. Yoshizuka, *Bull. Chem. Soc. Jpn.*, **66**, 2915 (1993).

6) K. Inoue, K. Ohto, K. Yoshizuka, R. Shinbaru, Y. Baba, and K. Kina, *Bunseki Kagaku*, **42**, 725 (1993).

7) K. Inoue, K. Ohto, K. Yoshizuka, R. Shinbaru, and K. Kina, *Bunseki Kagaku*, **44**, 283 (1995).