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Chelating Adsorbent for Heavy Metal Ions Prepared by Loading Anion-Exchange Resin with Thiacalix[4]arenetetrasulfonate

Hiroaki Matsumiya, Hideharu Masai, Yukiko Terazono, Nobuhiko Iki,* and Sotaro Miyano

Department of Biomolecular Engineering, Graduate School of Engineering, Tohoku University,
Aramaki-Aoba 07, Aoba-ku, Sendai 980-8579

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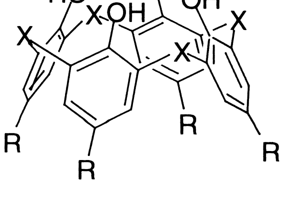
A chelating adsorbent for heavy metal ions has been prepared by loading an anion-exchange resin with thiacalix[4]arenetetrasulfonate (TCAS). Batchwise extraction studies have revealed a high adsorption ability of the TCAS-loaded resin toward heavy metal ions with high selectivity. The present resin strongly retained the heavy metal ions tested here [Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), and Pb(II)] in a slightly acidic to neutral pH region, while no adsorption was observed for alkaline earth metal ions, Mg(II) and Ca(II), in this pH region. These adsorption characteristics of the present resin should be ascribed to the contribution of the bridging sulfur of the loaded TCAS to selectively coordinate to metal ions categorized to be soft to intermediate Lewis acids by the Hard and Soft Acids and Bases (HSAB) rule. A continuous column adsorption system with the present resin allowed the selective and almost quantitative (more than 99.98%) removal of heavy metal ions.

Calixarenes, which are a class of macrocycles, generally made up of phenol units linked via methylene bridges, have been extensively investigated in various fields, especially metal ion- and molecular-recognition chemistry.[1] This undoubtedly relies on the feasibility of the calix-type molecular framework to be variously designed and modified by introducing proper ligating groups into the lower rim (the phenolic OH) and/or the upper rim (the *p*-position), which often makes calixarene a high-performance extractant of metal ions.[1–4] As one of the applications of such chemically modified calixarenes, several researchers have attempted to prepare selective chelating adsorbents by immobilizing them onto solid support materials.[5–8]

During the course of our continuing study on the functions of a new member of the calixarene family, "sulfur-bridged" calixarenes,[9] we have found that even the simplest one, *p-tert*-butylthiacalix[4]arene (TCA, see Fig. 1), itself, acts as an efficient extractant of transition metal ions,[10] which had been quite unexpected based on the poor extractability of the conventional calix[4]arene (CA) without any auxiliary ligating groups. The elucidated X-ray crystal structures of the metal-TCA complexes[11–14] clearly show the crucial role of the bridging sulfur to coordinate to the metal center with cooperative chelation of the adjacent phenolates O$^-$, thus providing another type of metal-binding site than that constructed by the above-mentioned conventional strategies, such as modifications at the aromatic rims to assemble pendent ligating groups.



	X	R
CA	CH_2	Bu^t
TCA	S	Bu^t
TCAS	S	SO_3^-

Fig. 1. Structures of calix[4]arenes.

Recently, we have succeeded to prepare a sulfonated analogue, thiacalix[4]arenetetrasulfonate (TCAS), in a satisfactory yield by direct sulfonation at the *p*-position of TCA.[15] As is well-known, chelating reagents having auxiliary ionic functional groups can be strongly retained onto common ion-exchangers through ionic bonds, thus providing a facile method to prepare selective chelating adsorbents.[16,17] The fact that TCAS contains four sulfonate groups in addition to the thiacalix-type metal-binding sites prompted us to prepare a chelating adsorbent by loading an anion-exchange resin with TCAS in view of the application to remove hazardous heavy metal ions from contaminated water. In this work, we thus have examined the adsorption characteristics of the TCAS-loaded resin for various heavy metal ions, compared with those for alkaline earth metal ions. The removal performance of the present resin for heavy metal ions has also been examined using a continuous column adsorption system.

Results and Discussion

Preparation of TCAS-Loaded Resin. As a support matrix, a commercially available strongly basic anion-exchange resin, Amberlite® IRA-900, was used, which comprised macroporous cross-linked polystyrene having trimethylammonium groups. The anion-exchange resin was easily functionalized with the chelating reagent, TCAS, by simply soaking the resin particle in an aqueous solution containing TCAS; the adsorption equilibrium was attained after 9 h. From the concentration of TCAS remaining in the aqueous solution after equilibrium, the content of TCAS in the resin was calculated to be 125 μmol per cubic-centimeter of swelling resin (hereafter, the volume of the resin is given as the apparent volume upon swelling with water).

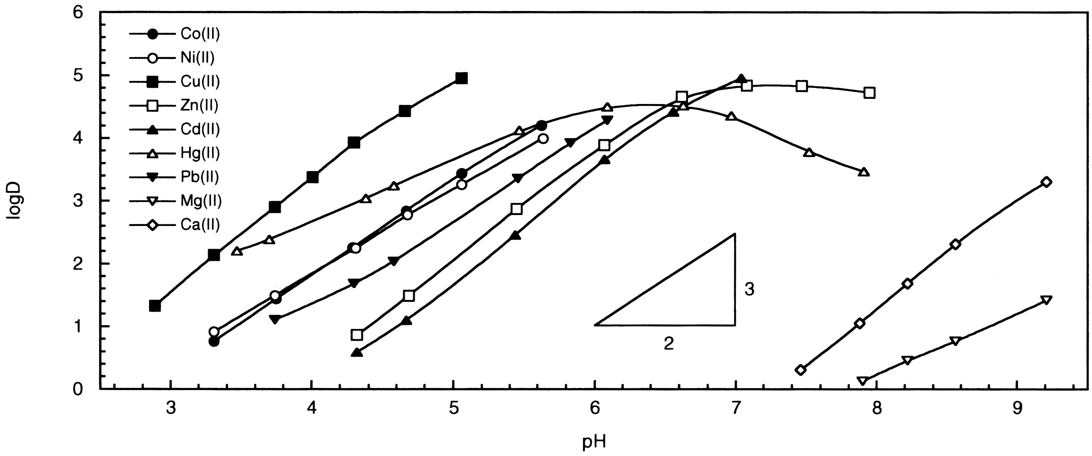


Fig. 2. The effect of solution pH on the equilibrium distribution ratio (D) for metal ions onto TCAS-loaded resin. TCAS-loaded resin: 0.80 cm^3. Volume of solution: 20.0 cm^3. Initial concentration of metal ions: 0.10 mmol dm^{-3}.

Distribution Studies. The metal-adsorption characteristics of the TCAS-loaded resin were examined by a conventional batchwise extraction method. In this work, the adsorption ability of the present resin was assessed by the distribution ratio (D), defined as the ratio of the concentration of the metal ion in the resin phase (mol cm^{-3}) to that in the aqueous phase (mol cm^{-3}), where the former was calculated from the change in the concentration of metal ion in the aqueous phase before and after a given soaking time. In any metal-adsorption process, no TCAS leaking out of the resin matrix was detected.

To examine the metal-adsorption characteristics of the TCAS-loaded resin, 7 kinds of heavy metal ions [Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), and Pb(II)] were selected together with 2 kinds of alkaline earth metal ions, Mg(II) and Ca(II). The resin matrix with no loaded TCAS possessed no capability to retain the metal ions in any pH region, except for Hg(II); a small blank adsorption of Hg(II) ($\log D$ = ca. 2) was observed irrespective of the solution pH, which may be caused by the complexation of Hg(II) with Cl$^-$, the counter anion of the trimethylammonium groups on the resin matrix, to form anionic complexes, such as $[HgCl_3]^-$ or $[HgCl_4]^{2-}$. In contrast, the TCAS-loaded resin strongly and selectively retained the heavy metal ions in a neutral pH region; the $\log D$ values for all of the heavy metal ions were over 4, around pH 6.5, while no adsorption of alkaline earth metal ions was observed under this pH condition (see Fig. 2).

The equilibrium distribution ratio of the metal ions generally increased with increasing in the solution pH, as the slopes in the linear range of the pH vs $\log D$ plots were approximately 3/2. This suggests that three protons should be released upon the adsorption of two metal ions, which is ascribable to the formation of 2:1 metal-TCAS complexes based on the following assumptions. Our detailed study on the solvent extraction of divalent transition metal ions with the parent compound TCA[10] suggested that TCA should bind to the metal center by coordination of the sulfide linkage and two adjacent phenoxide oxygens (see Fig. 3). Therefore, it can be assumed that TCAS has two chelating sites comprised of two phenol units linked by a sulfide bridge. Judging from the first pK_a value of TCAS (2.2),[18] one of the four phenolic OH groups in the loaded TCAS is considered to had already released its proton over the pH region tested (pH $>$ 3) in advance of complexation with metal ions. Therefore, the residual three phenolic OH groups should release their protons to coordinate metal ions as phenolates O$^-$ when the loaded TCAS forms a complex with two metal ions. Taking the Hard and Soft Acids and Bases (HSAB) rule[19] into consideration, the coordination of the bridging sulfurs is most likely to be specific to heavy metal ions. Such a contribution of the bridging sulfurs should be responsible for the selectivity of the metal-adsorption behavior of the TCAS-loaded resin. There is very little possibility that the sulfonate groups in the loaded TCAS take part in the metal-adsorption processes because it is a common understanding that the coordination ability of a sulfonate group is generally very poor. Furthermore, the sulfonate groups in the loaded TCAS should most probably be consumed by the immobilization of TCAS via ion-associations with the trimethlyammonium groups on the resin matrix.

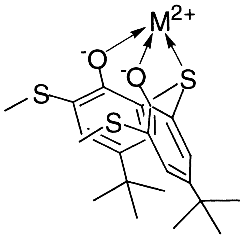


Fig. 3. Schematic view of the suggested coordination mode of TCA to divalent transition metal ions. For clarity, only half part of thiacalix-ring is depicted.

As shown in Fig. 4, the adsorption kinetics of metal ions was so fast that the log$D$ values exceeded 1.5 only at 10 min for all of the heavy metal ions tested. Equilibrium was attained within 15 h in all cases.

The metal ions retained on the TCAS-loaded resin were quantitatively desorbed by simply washing with a 0.5 mol dm^{-3} HNO_3 aqueous solution, except for the Hg(II) ion; the recovery of Hg(II) was 87%. Leaking of the loaded TCAS from the resin matrix was less than 0.01% during the metal-desorption processes.

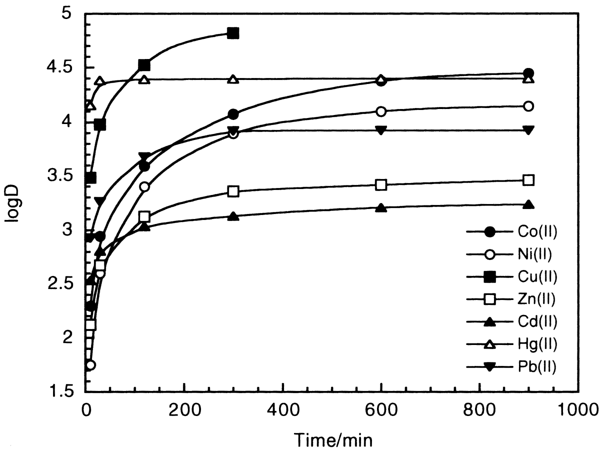


Fig. 4. Adsorption kinetics of heavy metal ions onto TCAS-loaded resin. TCAS-loaded resin: 0.80 cm^3. Volume of solution: 20.0 cm^3. Initial concentration of metal ions: 0.10 mmol dm^{-3}. Solution pH: 5.8.

Column Adsorption Experiments. The high adsorption ability of the TCAS-loaded resin toward heavy metal ions with a fast kinetic process is promising for the selective removal of heavy metal ions by a continuous column adsorption system. As shown in Fig. 5, at a practical feed rate (space velocity = 7.5 beds h^{-1}), a column packed with the TCAS-loaded resin strongly retained all of the heavy metal ions tested here [Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), and Pb(II)], while the alkaline earth metal ions [Mg(II) and Ca(II)] broke through the column immediately after the initiation of feeding the solution. In the best case, the break-through point, defined as the point where more than 1% metal ion in the feed solution leaked out of the column, was 460-fold of the bed volume for Hg(II) ion, which corresponds to the break-through capacity of 0.23 mmol cm^{-3}-resin. This value is close to the maximal capacity (0.25 mmol cm^{-3}-resin) calculated from the assumed stoichiometry of the TCAS complex (metal:TCAS = 2:1). Even in the worst case, the break-through point was still 88-fold of the bed volume for Ni(II) ion. However, at a rather fast feed rate (space velocity = 26 beds h^{-1}), the break-through points were generally reduced; especially for Co(II), Ni(II), and Zn(II), the break-through points were seriously reduced down to ca. 1/10 of those at a space velocity of 7.5 beds h^{-1}. As shown in Fig. 4, the adsorption kinetics of these metal ions was rather slower than those of the others. Therefore, the break-through capacity is likely to be controlled not only by the equilibrium adsorption capacity, but also by the adsorption kinetics. Before the break-through points, no leakage of fed metal ions was detected with an inductively coupled plasma atomic emission spectrometer (ICP-AES). This in turn means that the almost complete (more than 99.98%) removal of the heavy metal ions was successfully achieved, concerning the detection limits of the operated ICP-AES (0.01 μmol dm^{-3} for Cu to 0.1 μmol dm^{-3} for Pb).

Conclusion

We have shown here the high adsorption ability of the TCAS-loaded resin toward heavy metal ions with high selectivity, which most probably owes to the contribution of the bridging sulfur of the loaded TCAS to selectively coordinate to metal ions categorized to be soft to intermediate Lewis acids by the HSAB rule. The revealed high removal performance of the present resin in a continuous column adsorption system should be promising for the purification of water contaminated by heavy metal ions, especially highly hazardous ones, Cd(II), Pb(II), and Hg(II), in terms of the high removal ratio and break-through capacity.

Experimental

Measurements: A Horiba D-14 pH meter (Kyoto, Japan) equipped with a Horiba 6378-10D electrode was used for solution pH measurements. The concentration of metal ions was determined by a Seiko SPS-1200A inductively coupled plasma atomic emission spectrometer (Chiba, Japan). HPLC, consisting of a Shimadzu LC-9A pump unit (Kyoto, Japan), a Shimadzu SPD-10AV UV-VIS detector, and a Chromolith Performance RP-18e column (4.6 mm i.d. × 100 mm length; Merck KGaA, Darmstadt,

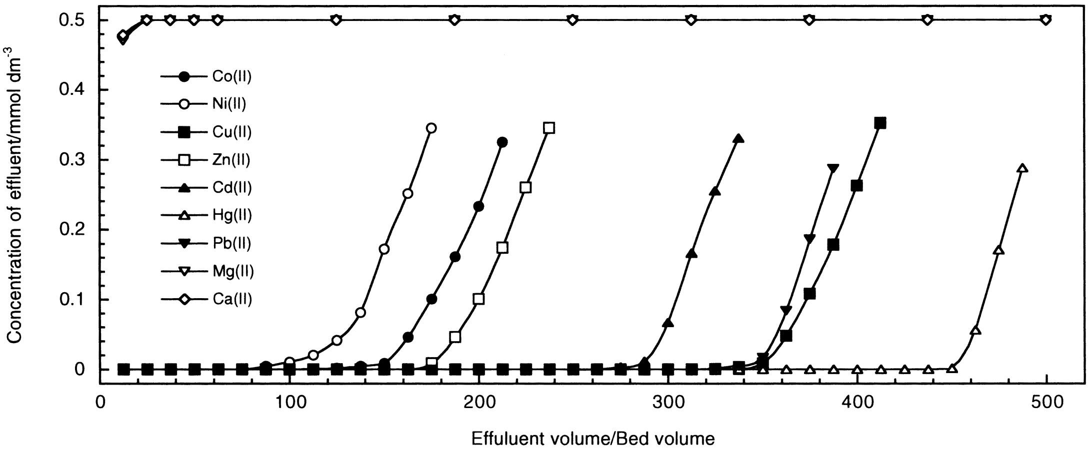


Fig. 5. Column breakthrough profile for the adsorption of metal ions by TCAS-loaded resin. Resin bed: 0.80 cm^3 (5.0 mm i.d. × 40 mm high). Concentration of metal ions in feed solution: 0.50 mmol dm^{-3}. Solution pH: 6.5. Feed rate: 0.10 cm^3 min^{-1} (7.5 beds h^{-1}).

Germany), was used in order to determine the concentration of TCAS [eluent, methanol–water mixture (2 + 3 m/m) containing tetra-*n*-butylammonium bromide (1.5 mmol kg^{-1}) and sodium acetate (5.0 mmol kg^{-1}); flow rate, 2.0 $\mathrm{cm}^3\ \mathrm{min}^{-1}$; detection wavelength, 310 nm].

Materials: The chloride form of a strongly basic anion-exchange resin, Amberlite® IRA-900 (Rhom & Haas, Philadelphia, PA, USA), was purchased from Taishin Chemical (Sendai, Japan). The chelating reagent, tetrasodium 25,26,27,28-tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene-5,11,17,23-tetrasulfonate (TCAS), was synthesized as described in the literature.[15] Stock solutions of metal ions (10 mmol dm^{-3}) were prepared by dissolving their nitrate salts in a 10 mmol dm^{-3} HNO_3 solution. All other reagents and solvents used were of guaranteed-reagent grade. Deionized water purchased from Daiwa Chemical (Sendai, Japan) was used throughout this study.

Preparation of TCAS-Loaded Resin: Amberlite® IRA-900 was ground and sieved to 80–230 dry-mesh size. The sieved resin (0.80 cm^3) was thoroughly washed with methanol and water, and then soaked in a 10.0 cm^3 of aqueous solution containing 10 mmol dm^{-3} of TCAS with stirring for over 10 h. Subsequently, the resin was filtered off, washed with water, and then conditioned in an appropriate pH buffer before used for following experiments.

Distribution Studies: A typical procedure was as follows. The TCAS-loaded resin (0.80 cm^3) was soaked in 20.0 cm^3 of a buffered solution containing 0.10 mmol dm^{-3} of metal ion with stirring for 18 h to reach equilibrium. Subsequently, after the resin was removed from the aqueous phase by filtration, the solution pH and concentration of the metal ions were determined.

Column Adsorption Experiments: A feed solution containing 0.50 mmol dm^{-3} of metal ion at pH 6.5 was continuously passed through a glass column (5.0 mm i.d. × 50 mm length) packed with the TCAS-loaded resin (0.80 cm^3). The feed rate was adjusted to be 0.10 $\mathrm{cm}^3\ \mathrm{min}^{-1}$, which corresponded to a space velocity of 7.5 beds h^{-1}. The effluent fractions were collected in 10 cm^3 portions, and the concentration of metal ions was determined.

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