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Adsorption and desorption method for cacodylic acid with inorganic ion exchangers

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Synthetic inorganic ion exchangers were studied regarding adsorption and desorption features of cacodylic acid $[(CH_3)_2A_3O(OH)]$ with a view to finding a selective adsorbent in aqueous solution. Hydrous oxides of titanium [Ti(IV)], Zirconium [Zr(IV)], manganese [Mn(IV)] and ion [Fe(III)] among synthetic inorganic ion exchangers showed a high selectivity towards cacodylic acid over a wide pH range lower than 12. A large capacity for cacodylic acid (1.0 mmol g^{-1}) was observed for amorphous hydrous titanium dioxide (Am-HTDO) at pH$<$5.5 in a solution of ionic strength of 0.1 made with (NaCl+HCl) or (NaCl+NaOH). The uptake by the column method (0.9 mmol g^{-1}) was in good agreement with the batch method. The acid could be quantitatively eluted by 1 mol dm^{-3} NaOH.

Keywords: Cacodylic acid, inorganic ion exchanger, adsorption, hydrous oxides, environmental pollutant

INTRODUCTION

Synthetic inorganic ion exchangers have been reported to show an excellent selectivity towards some metal ions.[1-5] Particularly, oxides and hydrous oxides of multivalent metals have a relatively large ion-exchange capacity and an excellent ion-exchange selectivity towards certain cations.[6-16] These inorganic ion-exchange materials have found applications for the selective separation of cations in the fields of hydrometallurgy, ratioanalytical chemistry, environmental chemistry and biochemistry.

Organometallic compounds and oxides of heteroelements, e.g. arsenic, tin, selenium, tellurium, etc., are widely used in industry, biomedical fields, agriculture and the marine product industry. Recently, environmental pollution by these materials appears to be occurring. Discharged organometallics are possibly transformed to more toxic oxoanions via microbial action in an aqueous environment and vice versa.[17] Adsorption methods using selective adsorbents may be expected to be effective for the prevention of all effects due to the discharge of these toxic materials to various environments.

The following adsorption features are required for a candidate for effective separation of cacodylic acid (pK_a6·2), which forms anions at a relatively high pH.

(a) Selectivity for cacodylic acid in low concentration at around neutral pH.
(b) A large adsorption capacity for cacodylic acid.
(c) The adsorped cacodylic acid can be eluted by a suitable eluent with a reasonable rate of desorption.
(d) Sufficient physical strength to make a granular material for the column.
(e) Little toxicity.

Several different types of synthetic inorganic ion exchangers are known:[2-4] for example hydrous oxides and acid salts of multivalent metals [$TiO_2 \cdot nH_2O$, $Zr(HPO_4)_2 \cdot H_2O$, etc], salts of heteropolyacids, insoluble ferrocyanides, synthetic aluminosilicates, apatites. Of these, insoluble hydrous oxides of multivalent metals will be advantageous because of lower toxicity and solubility. These behave as anion exchangers at low pH and as cation exchangers at high pH. The critical point is given by the equiadsorption point (EAP). The EAP is defined by the pH at which equal uptake for potassium (K^+) and chloride (Cl^-) ions takes place.[6] The EAP of hydrous oxides varies linearly with the ionic potential (Z/r) of the metal ion (Z=formal charge, r=crystal ionic radius).[6, 18] In addition, the ion-exchange selectivity for ions in synthetic inorganic ion exchangers is strongly dependent on the shape

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and dimensions of the ion-exchange cavity which imposes steric limitations.

The present work was carried out with a view to finding a selective adsorbent for cacodylic acid among some synthetic ion exchangers and organic ion-exchange resins.

EXPERIMENTAL

Ion-exchange materials

The inorganic ion exchangers below (a–e) were synthesized according to methods reported earlier. A brief description of the synthetic method and the chemical composition are given below. These exchangers were identified by thermal studies (thermogravimetric and differential thermal analysis, TG and DTA) and X-ray diffraction with Ni-filtered CuKα radiation, except for hydrous manganese(IV) oxide in which case Mn-filtered FeKα radiation was used.

(a) Hydrous titanium dioxide (amorphous form): $TiO_2 \cdot 2.3H_2O$[15]

Liquid $TiCl_4$ (100 cm^3) was prehydrolyzed by adding slowly demineralized water (300 cm^3). The resultant clear solution was hydrolyzed by adding dropwise 2.8 mol dm^{-3}-NaOH (1600 cm^3) with vigorous stirring. The precipitate formed was precolated, washed thoroughly and air-dried. The semi-transparent product was ground and sieved to 100–200 mesh. Incorporated sodium ion within it was removed as much as possible by percolating 0.1 mol dm^{-3}-HNO_3 as an eluent through the column. The product was then washed with water and air-dried.

(b) Hydrous manganese (IV) oxide (cryptomelane-type): $MnO_2 \cdot 0.45H_2O$[9]

A precipitate was formed by slowly adding 0.5 mol dm^{-3} $KMnO_4$ solution in 1 mol dm^{-3} H_2SO_4 (200 cm^3) to 200 cm^3 of 1 mol dm^{-3} $MnSO_4$ solution in 1 mol dm^{-3} H_2SO_4 at 60°C, and aged overnight in the mother liquor. The precipitate was washed with 6 mol dm^{-3} HNO_3 (500 cm^3) and then washed with water until pH of washings >2. It was dried at 70°C in an oven for three days, ground and sieved to 100–200 mesh. Incorporated potassium and sulphate ions in the solid were removed as much as possible with concentrated HNO_3 as an eluent using the column method. The flow rate of concentrated HNO_3 used was 0.1 cm^3 min^{-1} and finally the potassium ion concentration in the effluent was lower than 10^{-5} mol dm^{-3}. After washing thoroughly with water, the solid was air-dried and used.

(c) Iron (III) oxide hydroxide (β-type): $FeOOH \cdot 0.2HCl \cdot 0.2H_2O$[2]

$FeCl_3 \cdot 6H_2O$ (540 g) was dissolved in 20 litres of demineralized water to prepare 0.1 mol dm^{-3} Fe(III) solution. It was hydrolyzed to form hydrous iron oxide by heating the solution at 70°C for 24 h. The precipitate was aged in the mother solution for one day and percolated. The precipitate was washed until pH 3 with 0.25 mol dm^{-3} NaCl solution centrifuged at 10000 rpm to prevent a formation of colloid. It was air-dried at room temperature for 3 days ground and sieved to 50–100 mesh. It was washed with water until the concentration of chloride ion in the washings became nearly constant (0.01 mol dm^{-3}), and then air-dried.

(d) Hydous zirconium oxide (amorphous form): $ZrO_2 \cdot 1.76H_2O$

This was prepared by the sol–gel method: zirconium tetrabutoxide, $Zr(OBu)_4$, was added dropwise to water to allow formation of a precipitate. The precipitate was washed thoroughly, filtered under suction, air-dried and then sieved to 100–200 mesh.

(e) Hydrous aluminium oxide (boehmite-type): $Al_2O_3 \cdot 1.2H_2O$[2]

Aqueous 4 mol dm^{-3} ammonia solution (NH_3aq) was added to aqueous 10% $AlCl_3$ solution to form a precipitate up to pH 8–10. The precipitate was washed repeatedly with aqueous ammonia (0.1 mol dm^{-3}) of pH 9 until free from chloride ion, and then aged for 30 days at room temperature in aqueous ammonia solution of pH 9. After washing, it was hydrothermally heated for 5 h at 200°C, air-dried and sieved to 100–200 mesh.

(f) Hydrotalcite (Kyowaad 500): $Mg_6Al_2(OH)_6CO_3 \cdot 4H_2O$

This was supplied by Kyowa Chemical Industries.

All other chemicals were of analytical grade and supplied by Wako Pure Chemical Industries Ltd.

Chemical analysis

Arsenic and other heavy metal ions were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Seiko

Instruments Inc. model SPS7000 instrument, or by neutron activation analysis (NAA) at the Japan Atomic Energy Research Institute. For the latter method, a 25–50 μL aliquot of a sample solution was taken on a small piece of filter paper (1 cm × 2 cm), sealed into polyethylene and irradiated along with the standard solution. The γ-spectrometry was carried out using a Cambera multichannel analyzer MCA-30. Sodium and chloride ions were determined by flame photometry with a Varian 1100 spectrometer and by argentometry respectively.

Selectivity study by a batch method

A 0.250 g or 0.100 g samples of exchanger was equilibrated with 25 cm^3 or 10 cm^3 of solutions containing various concentrations of arsenic compounds with ionic strength 0.1 or 0.01 (by NaCl and/or HCl). The equilibrium pH and arsenic concentration were determined after equilibration at 30°C. The distribution coefficient K_d was defined by the equation:

$$K_d = \frac{\text{amount of arsenic compound absorbed}}{\text{concn of arsenic compound in soln}} \times \frac{\text{vol. of soln}}{\text{wt of exchanger}} \quad [1]$$

Sorption–desorption study by the column method

The column capacity was determined by injecting into a column an arsenic compound solution of pH4 (2×10^{-2} mol dm^{-3} as arsenic) with the ionic strength adjusted to 0.1 (by NaCl + HCl or NaCl + NaOH). After saturation, the column was washed by a small amount of 0.1 mol dm^{-3} NaCl solution of pH4, and then sorbed arsenic species were eluted by 0.1 mol dm^{-3} NaOH solution. The adsorbed or desorbed amounts were calculated from the areas of breakthrough or elution curves.

RESULTS AND DISCUSSION

Inorganic ion-exchange materials

The chemical composition and the crystal data were in good agreement with those reported previously.

Selectivity study for arsenic compounds

Ion-exchange rates of cacodylic acid and inorganic arsenic acids [As(V) and As(III)] were studied on hydrous manganese(IV) dioxide and hydrous titanium dioxide as representatives (Fig. 1). It was found that equilibrium was attained within 5 days for both ion exchangers.

Uptake for three arsenic compounds was studied on inorganic ion exchangers (Fig. 2). A commercially available hydrotalcite and a synthesized ferric oxide hydroxide known to be an anion exchanger showed a low selectivity for cacodylic acid, although they showed a high selectivity towards arsenic and arsenious acids in low concentrations ($<10^{-3}$ mol dm^{-3}). Hydrous aluminium oxide and hydrous zirconium dioxide had a relatively small capacity for cacodylic acid <0.2 mmol g^{-1}). On the contrary, hydrous manganese(IV) oxide (sample **b**) and hydrous titanium dioxide (sample **a**) showed a relatively large capacity (>0.3 mmol g^{-1}) at pH range studied. These were studied in more detail in the following experiment.

The pH dependence for uptake of three arsenic compounds was studied on the two ion exchangers (Fig. 3). Sample **b** showed the following uptake: 0.7 mmol g^{-1} for arsenious acid at pH 6.8, 0.4 mmol g^{-1} for arsenic acid at pH$<$6

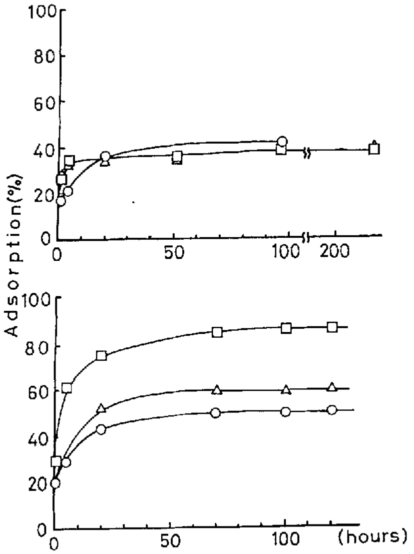

Figure 1 Time dependence of adsorption of three arsenic compounds. Initial concn 0.02 mmol dm^{-3} for sample **a** (below) and 0.01 mmol dm^{-3} for sample **b** (above). ○, Cacodylic acid; △, As(V); □, As(III); volume of solution 25 cm^3. Exchanger, 0.250 g. Temperature, 30°C. Ionic strength, 0.01 with NaCl.

and 0.3 mmol g^{-1} for cacodylic acid at pH 5–6. Sample **a** had a larger uptake for these arsenic compounds than sample **b**. Uptake for cacodylic acid indicated a nearly constant uptake (1.0 mmol g^{-1}) at pH<5.5 and decreased to zero uptake at pH 8. Uptake for arsenic acid decreased approximately linearly with increase in pH and was zero at pH 10.5. Arsenious acid showed the maximum uptake of 1.8 mmol g^{-1} at a pH around 8. Thus, sample **a** was found to be a promising adsorbent towards cacodylic acid at pH<5.5.

Ion-exchange selectivity for arsenic compounds

The EAP of sample **a** was located at pH 4.2 (Fig. 4a). Arsenic compounds are adsorbed along with sodium ions at a pH region where they are present as anions (Fig. 4b–d). Their dissociation constants (pK_a) are given as follows: $(CH_3)_2AsO(OH)$, pK6.2 (25°C); $AsO(OH)_3$, pK_1 2.22, pK_2 6.98 and pK_3 11.50 (25°C); $As(OH)_3$, pK 9.06 in 0.1M-KCl(30°C).[19] These compounds are better adsorbed at lower pH. The pH of the solution was shifted to higher values after equilibration (Table 1). This suggests that the adsorption of arsenic compounds may be represented by the following equations, depending on the pH.

$$\text{At low pH: } \equiv\text{Ti—OH} + \text{HA} \rightleftharpoons \equiv\text{Ti—OH}_2{}^+\text{A}^- \qquad [2]$$

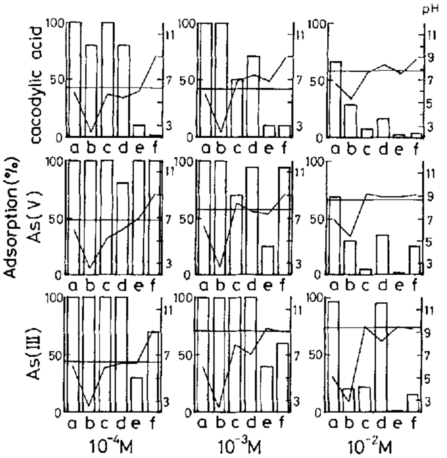

Figure 2 Adsorption profile for three arsenic compounds on inorganic ion exchangers a–f. Volume of solution 10 cm^{-3}. Exchanger, 0.10 g. Temperature, 30°C. Ionic strength, 0.01. Equilibration time, 5 days. Horizontal line shows the initial pH. The equilibrium pH was connected by the zigzag line.

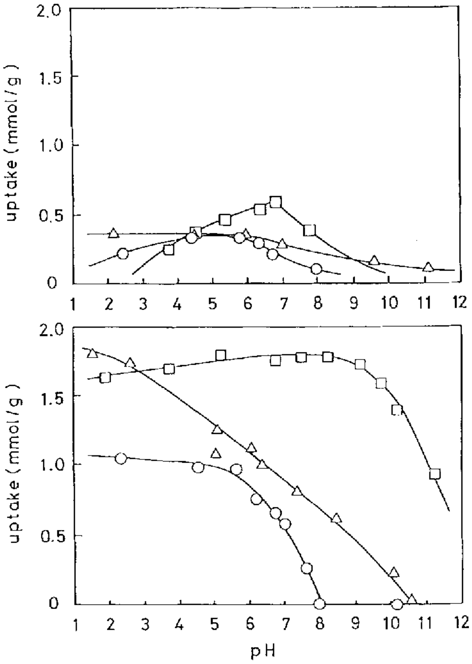

Figure 3 pH dependence of uptake for three arsenic compounds on sample **a** (below) and sample **b** (above). Initial concn 0.02 mmol dm^{-3}, 10 cm^3. Exchanger, 0.10 g. Temperature 30°C. Ionic strength, 0.10. Symbols are the same as for Fig. 1.

$$\text{or } \equiv\text{Ti—A} + \text{H}_2\text{O} \qquad [3]$$

$$\text{At high pH: } \equiv\text{Ti—OH} + \text{A}^- + \text{H}_2\text{O} \rightleftharpoons \equiv\text{Ti—OH}_2{}^+\text{A} + \text{OH}^- \qquad [4]$$

If the absorption of the species A^- obeys Eqn [4], the plot of log K_d vs pH should indicate a slope of −1, as shown in the following. The thermodynamic constant, K, and the K_d are defined by:

$$K = \frac{\overline{[A^-]}\,[OH^-]\,f_A\gamma_{OH}}{\overline{[OH^-]}\,[A^-]\,f_{OH}\gamma_A};\quad K_d = \frac{\overline{[A^-]}}{[A^-]} \qquad [5]$$

where the bar on the character denotes the solid, f the activity coefficient of species in the solid and γ the activity coefficients of species in the solution. If $\overline{[A^-]} \ll \overline{[OH^-]}$, $[A^-] \ll [OH^-]$ and $\overline{[OH^-]}$ is nearly constant, we can deduce

$$\log K_d = C - \text{pH} \qquad [6]$$

where C is given by

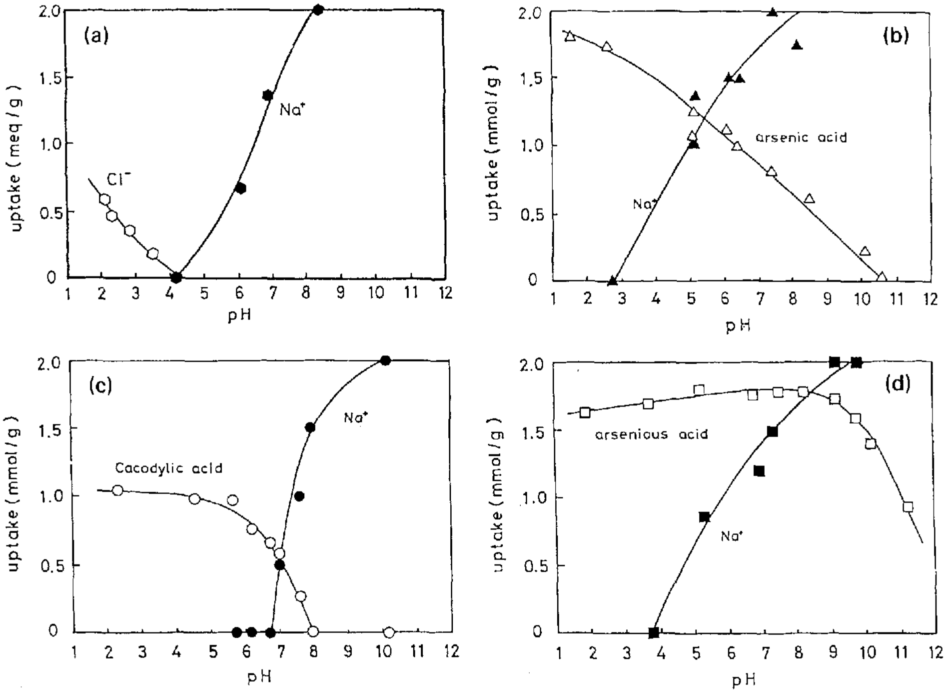

Figure 4 Uptake of Na$^+$ and arsenic compounds on sample **a** as a function of pH. Initial concentration of arsenic compounds 0.02 mmol dm^{-3}. Volume of solution, 10 cm^3. Exchanger, 0.10 g. Temperature 30°C. Ionic strength, 0.10.

$$C=\log[\overline{\mathrm{OH}}]\frac{f_{\mathrm{OH}}\gamma_A}{f_A\gamma_{\mathrm{OH}}}\frac{K}{K_{\mathrm{W}}} \qquad [7]$$

and K_{W} is the ionic product of water.

The plot of log K_d vs pH for arsenic(III) ions showed a slope of −1.1 at pH 7–10 and −0.2 at pH > 10 for sample **b** (Fig. 5a). Those for arsenic (V) ions showed a slope of −0.5 at pH 7–11 and −0.2 at pH > 11. Adsorption for these arsenic compounds was partially reversible, as indicated by the solid symbols. The slope for $(CH_3)_2AsO(OH)$ was −0.85 and it is a reversible ion-exchange process. On the other hand, a plot of log K_d vs pH for sample **a** showed a similar slope for three arsenic compounds (Fig. 5b): −0.92 for arsenic(III) at pH > 9.5, −0.85 for

Table 1 pH change with adsorption of cacodylic acid on sample **a**

Conditions are given in the legend to Fig. 4.

pH		Uptake of cacodylic acid (mmol g^{-1})	Na$^+$ uptake (mmol g^{-1})
Init.	Equil.		
2.28	2.32	1.04	0
3.52	4.56	0.985	0
6.10	6.20	0.753	0
6.78	6.72	0.655	0
7.80	7.00	0.58	0.5
11.80	7.65	0.267	1.0
12.30	10.15	<0.01	2.0

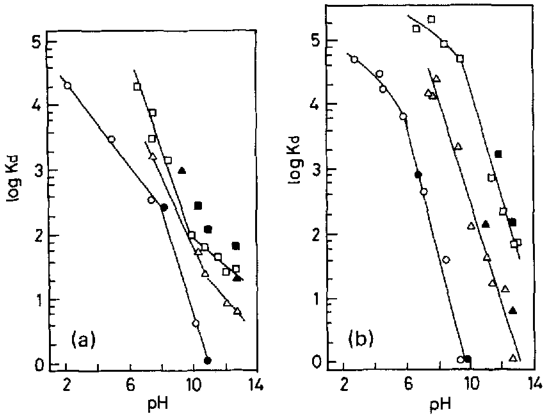

Figure 5 Ion-exchange ideality and reversibility for exchange adsorption of arsenic compounds on samples **a**(b) and **b**(a). Initial concentration, 1.0 × 10^{-4} mol dm^{-3}. Volume of solution, 10 cm^3. Exchanger, 0.10 g. Temperature, 30°C. Ionic strength, 0.10. Symbols are the same as for Fig. 1.

arsenic(V) at pH>7.5 and −0.96 for cacodylic acid at pH>6. In these pH ranges and concentrations, the predominant chemical species are mononuclear $As(OH)_4^-$, $AsO_3(OH)^{2-}$, and $(CH_3)_2AsOO^-$. Therefore, ion exchange for $As(OH)_4^-$ and $(CH_3)_2AsOO^-$ is 'ideal' and reversible in these conditions. However, the slope for $AsO_3(OH)^{2-}$ was different from the expected value. A lower concentration of $AsO_3(OH)^{2-}$ may be required for the 'ideal' exchange.

Chromatographic separation of cacodylic acid

A nearly constant uptake (1.0 mmol g^{-1}) for cacodylic acid was observed at pH<5.5 when the initial concentration was 2×10^{-2} mol dm^{-3}, as described above. In order to get an optimum design for the chromatographic separation, the ion-exchange isotherms for three arsenic compounds were measured at around pH 4, which is the EAP of sample **a** (Fig. 6). A very steep rise was observed for the three arsenic compounds studied in the early stage of uptake. Arsenic(V) and cacodylic acids showed the maximum uptake, 1.4 and 1.2 mmol g^{-1} at 2×10^{-2} mol dm^{-3}. Uptake for arsenic(III) acid increased with an increase in the concentration and showed a large uptake of 3.3 mmol g^{-1} at 2.7×10^{-2} mol dm^{-3}.

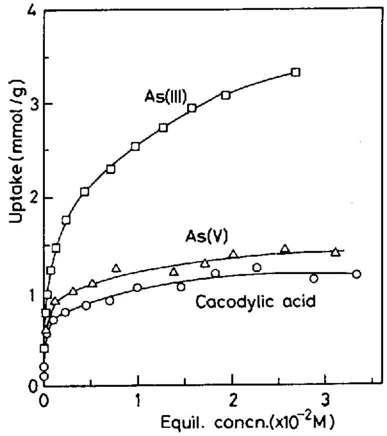

Figure 6 Ion-exchange isotherms for arsenic compounds on sample **a**. Volume of solution 10 cm^3. Ionic strength, 0.10. Exchanger, 0.10 g. Temperature, 30°C. Equilibrium pH, 4–5.

The areas between the breakthrough curve and the blank curve gave uptakes of 0.91, 0.90 and 2.28 mmol g^{-1} for cacodylic, arsenic(V) and arsenic(III) acids respectively (Fig. 7a, c, e). Those for cacodylic and arsenic(V) acids are of a sigmoidal shape with a steep rise in the breakpoint. That for arsenic(III) showed a slow increase in the concentration of the effluent, which may be attributed to a relatively low rate of particle diffusion. The predominant chemical species are monomeric $(CH_3)_2AsO(OH)$, $AsO_2(OH)_2^-$ and

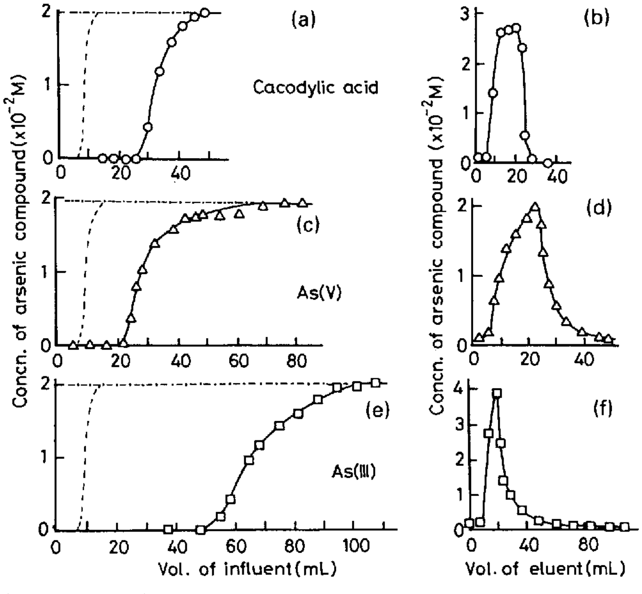

Figure 7 Breakthrough (left) and elution (right) curves for arsenic compounds. Dotted line, blank curves. Column, 2.5 cm × 0.5 cm diam. (sample **a**, 0.5 g, 100–200 mesh). Concentration of influent, 0.020 mol dm^{-3} (pH 4 by HCl). Ionic strength, 0.10 with NaCl. Flow rate, 0.05 cm^3 min^{-1} for cacodylic acid, 0.2 cm^3 min^{-1} for As(V) and As(III) acids.

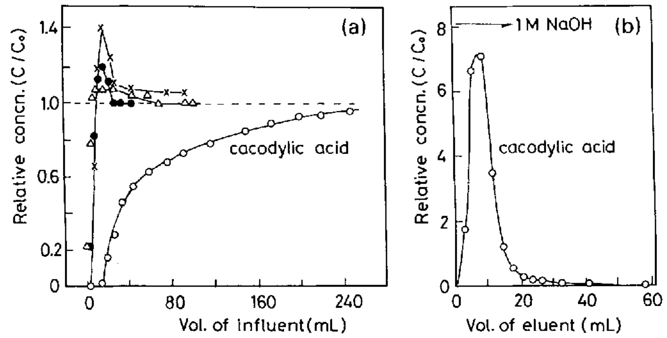

Figure 8 Breakthrough (inflexion) (left) and elution (right) curves for real waste. Column: 10 cm × 0.5 cm diam. (sample **a**, 2.0 g, 100–200 mesh). Flow rate, 0.10 $cm^3 min^{-1}$. Solution and concentration (C_0) are given in Table 2. ○, Cacodylic acid; ×, Os; ●, Fe; △, Cu.

Table 2 Elemental composition of cacodylic acid waste (in 10^{-1} mmol dm^{-3}).

sample	Hg	Cr	Cd	As	Pb	Cu	Mn	Zn	Fe	Ni	Co	Sn
No. 1	*	*	*	930	*	*	*	*	*	1.1	*	*
No. 2	*	2.5	*	173	1.4	4.4	*	5.8	3.22	*	*	*

*, <5 $\mu g\ cm^{-3}$

$As(OH)_3$ in a solution of <0.1 mmol dm^{-3} at pH ~ 4[19]. However, arsenic (III) is polymerized in the higher concentration. Within sample **a**, the concentration of arsenic (III) will attain 2–3 mol dm^{-3}, and so arsenic (III) is possibly exchanged in the polymerized species. It may be responsible for the slow uptake.

These adsorbed arsenic compounds could be eluted by 0.1 mol dm^{-3} NaOH with yields of 85%, 73% and 51% for cacodylic, arsenic(V) and arsenic(III) acids respectively (Fig. 7b, d, f). The small fraction of elution for arsenic(III) is attributed to the high selectivity, as shown in the isotherm. A higher concentration of sodium hydroxide (NaOH) is necessary for the complete elution of adsorbed arsenic(III).

The adsorption features of sample **a** described above will enable a separation of cacodylic acid from aqueous solutions. The chemical composition of a waste solution supplied by Kyoto University is given in Table 2. It contains cacodylic acid at a concentration of 1300 ppm along with other heavy metals, osmic acid and a small amount of sucrose and aldehydes. The waste solution is black, due to the presence of osmium [Os(VI)]. Cacodylic acid adsorbed was 0.560 mmol g^{-1} (Fig. 8a) and was quantitatively eluted (0.566 mmol g^{-1}) with 1 mol dm^{-3} NaOH as an eluent after washing with a small amount of water. The effluent was pale orange and contained almost no osmic acid and other heavy metals. Heavy metals other than zinc were not adsorbed, probably because of complexation with organics.

Thus, sample **a** was demonstrated to be effective for the separation of cacodylic acid from real waste. After elution with 1 mol dm^{-3} NaOH, adsorbed sodium ion can be eluted and the column can be used repeatedly.

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