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Behavior of a Methylenephosphonic Acid Chelating Resin in Adsorption and Elution of Molybdenum(VI)

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ABSTRACT

The behavior of a chelating resin RCSP, macroreticular styrene–divinylbenzene copolymer-based methylenephosphonic acid resins, in the adsorption and desorption of molybdenum(VI) was studied. The resin exhibits the maximum uptake of molybdenum(VI) as high as 3 mmol/g around pH 1, and no uptake in the pH region higher than 7. Thus, molybdenum(VI) adsorbed on RCSP from acidic solutions was quantitatively eluted with aqueous sodium hydroxide as well as with aqueous sodium acetate, indicating the promising use of the resin in the separation of molybdenum(VI) from other metal ions.

INTRODUCTION

It has been shown that organophosphorous acids are useful for the separation of Mo(VI) by means of the solvent extraction technique (1–4); Mo(VI) is successfully extracted into organic phases with these extractants from strongly acidic media. Based on these phenomena, it is expected that chelating resins containing phosphorous acid groups will be able to adsorb Mo(VI) from strongly acidic media. Although recent work reported by Egawa et al. (5–7) and by Alexandratos's group (8–14) has revealed

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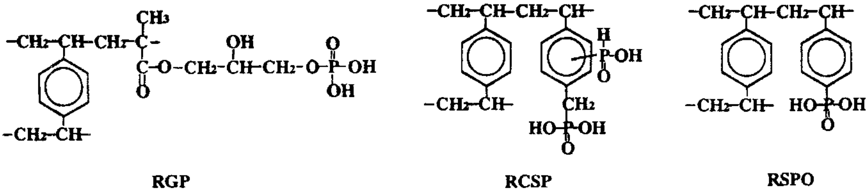

SCHEME 1 Structures of the resins. RGP and RCSP are macroreticular-type resins and RSPO is gel-type one.

that chelating resins having phosphorous acid groups exhibit selectivity toward metal ions with high oxidation states, such as lanthanides(III), Fe(III), Cr(III), Ga(III), In(III), U(VI), Np(IV), and Am(III), the behavior of these resins toward Mo(VI) has not yet been studied.

Mo(VI) species dissolved in aqueous media exist as the monomeric MoO_4^{2-} in basic solutions, but various polymerized species, such as $Mo_7O_{24}^{6-}$, $HMo_7O_{24}^{5-}$, and $H_2Mo_7O_{24}^{4-}$, are successively formed with decreasing pH of solutions (15, 16). Thus, it can be predicted that the porosity of resins will have a significant meaning in the uptake of Mo(IV), in particular in dynamic adsorption. Consequently, this work began with the column-mode adsorption of Mo(VI) by using resins of both the gel and macroreticular types (Scheme 1). Among the resins tested, RCSP exhibited the highest columnar performances. Therefore, the behavior of RCSP in the adsorption and elution of Mo(VI) was then studied in detail.

EXPERIMENTAL

Materials

Resins RSPO, RCSP, and RGP were prepared according to previously reported methods (5, 17, 18). The properties of these resins are summarized in Table 1. These resins were used in their hydrogen form, and their particle sizes were from 32 to 60 mesh in the dry state, unless otherwise noted. Stock solutions of Mo(VI) were prepared from sodium molybdate. Other chemicals were of reagent grade.

Columnar Adsorption of Mo(VI)

Each wet settled resin (bed volume = 1 mL) was placed in a fritted glass column (0.7 cm inner diameter, 10 cm length). In adsorption of Mo(VI), a solution containing Na_2MoO_4 (0.01 M) and H_2SO_4 (0.5 M) was supplied

TABLE 1
Properties of Chelating Resins in Hydrogen Ion Form

Resin	Cation exchange capacity meq/g	Cation exchange capacity meq/mL	Phosphorus content (mmol/g)	Specific surface area (m^2/g)	Dry volume (mL/g)	Wet volume (mL/g)
RCSP[a]	7.2–7.4	2.5–2.8	4.0–4.3	19–25	1.8–2.0	2.8–2.9
RSPO[b]	8.7	3.3	4.2	0	1.3	2.6
RGP[c]	7.0	2.1	3.4	28	2.1	3.3

[a] Derived from styrene–divinylbenzene copolymer beads prepared by using 10 mol% of divinylbenzene and 100 vol% of diluent (2,2,4-trimethylpentane) per monomeric mixture.

[b] Gel-type resin. Derived from styrene–divinylbenzene copolymer beads prepared by using 10 mol% of divinylbenzene.

[c] Derived from glycidyl methacrylate–divinylbenzene copolymer beads prepared by using 10 mol% of divinylbenzene and 140 vol% of diluent (isobutyl acetate) per monomeric mixture.

to the column at an hourly rate of 10 bed volumes until the column effluent concentration became equal to the feed concentration. After washing with 10 bed volumes of 0.5 M H_2SO_4, Mo(VI) on the column was eluted with 1 M NaOH at an hourly rate of 3 bed volumes. All column effluents, including the washing, were collected on a fraction collector, and the Mo(VI) concentration in each fraction was determined by means of inductively coupled plasma atomic emission spectrometry (ICP-AES).

Batchwise Adsorption of Mo(VI) with RCSP

The capacity for uptake of Mo(VI) was evaluated by the following method. The resin (0.1 g) was placed with 0.01 M sodium molybdate solution (50 mL) in a 100-mL Erlenmeyer flask and shaken for 24 hours at 30°C. The solution was then filtered and its metal ion concentration determined by ICP-AES. In the measurement of distribution ratios, 0.04 g of the resin and 25 mL of 0.0001 M sodium molybdate solution were used, and the followed procedures were almost the same as those in the capacity measurement. The distribution ratio (D), designated by the relation $D = C_r/C_s$, was calculated; here, C_r and C_s stand for amounts of Mo(VI) in the resin and solution phases at the equilibrium, respectively. The pH of the test solutions (pH from 1 to 11.5) was adjusted with HCl or NaOH. The effect of acid species on Mo(VI) uptake was examined using HCl, HNO_3, H_2SO_4, and H_3PO_4.

Elution of Mo(VI) Adsorbed on RCSP with Aqueous NaCl and CH_3COONa

Wet settled RCSP (bed volume = 2 mL) was placed in a fritted glass column (1 cm diameter, 20 cm length), and then Mo(VI) was loaded to the column by feeding 150 mL of a solution containing Na_2MoO_4 (0.01 M) and H_2SO_4 (0.05 M) at an hourly rate of 10 bed volumes. The stepwise elution was conducted by successively supplying 0.1, 0.5, and 1 M solutions of CH_3COONa or NaCl (20 bed volumes of each solution). Elution with only 0.5 M CH_3COONa was also conducted.

RESULTS AND DISCUSSION

Columnar Adsorption of Mo(VI)

Figure 1 shows the column-mode adsorption of Mo(VI) by the resins RGP, RCSP, and RSPO from 0.5 M H_2SO_4. Amounts of Mo(VI) adsorbed on the RGP, RCSP, and RSPO columns were 0.38, 0.70, and 0.78 mmol/mL of wet resin, respectively. The Mo(VI) uptake increases in the order RGP < RCSP < RSPO. This order coincides with the increasing order

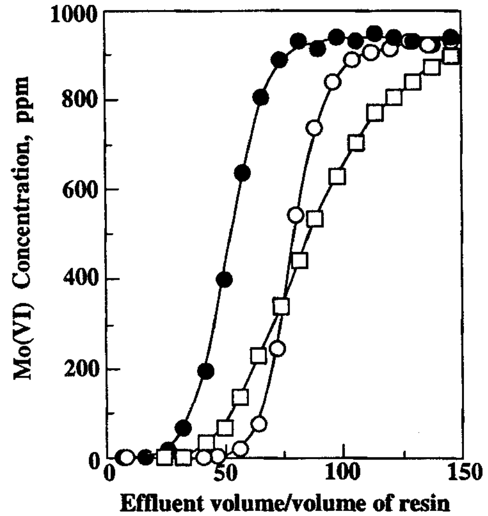

FIG. 1 Loading curves for molybdenum(VI): (●) RGP, (○) RCSP, (□) RSPO. The sizes of RCSP used here were 60–80 mesh.

of cation-exchange capacities or phosphorus contents of the resins (Table 1). On the other hand, breakthrough capacities for Mo(VI) are not correlated to the cation-exchange capacities; the capacities of the RGP, RCSP, and RSPO columns are ca. 0.2, 0.5, and 0.3 mmol/mL of wet resin, respectively. The shapes of the breakthrough curves clearly indicate that RGP and RCSP take up Mo(VI) much more rapidly than does RSPO. As judged from the specific surface areas given in Table 1, RCSP and RGP have macroreticular structures but RSPO does not. Thus, the macroreticular structure is essential to the rapid uptake, since Mo(VI) tends to form bulky polymerized species (15, 16). The gel-type matrix of RSPO is probably not suitable for rapid diffusion of the bulky polymerized species of Mo(VI). Molybdenum(VI) adsorbed on the RGP, RCSP, and RSPO columns was quantitatively eluted with 1 M NaOH as shown in Fig. 2. Opposed to the case of adsorption, no marked differences in the elution rates were observed among the tested resins. In alkaline solutions, Mo(VI) exists as a monomeric species, MoO_4^{2-} (15, 16), so that the elution rate with NaOH may not be so sensitive to the porosity of the resins. Based on the results mentioned above, the further detailed study was limited to RCSP.

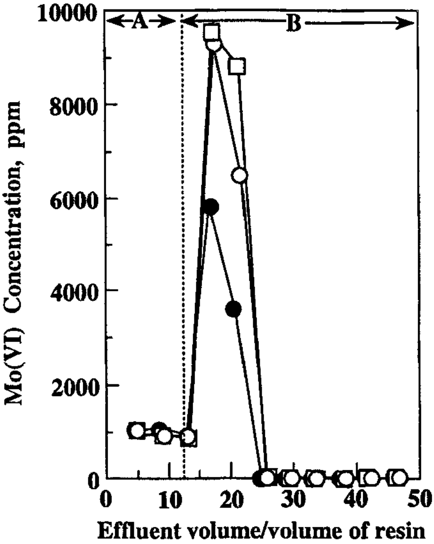

FIG. 2 Elution of molybdenum(VI) with 1 M sodium hydroxide. The sizes of RCSP used here were 60–80 mesh. (●) RGP, (○) RCSP, (□) RSPO. (A) Washing with 0.5 M H_2SO_4. (B) Elution with 1 M NaOH.

Batchwise Adsorption of Mo(VI) with RCSP

Figure 3 shows the relationship between equilibrium pH and Mo(VI) uptake. Above pH 7, RCSP cannot adsorb Mo(VI), and Mo(VI) uptake increases with decreasing pH. This is quite the reverse of the tendency observed in the uptake of most metal ions, such as Fe(III), U(VI), Ca(II), and lanthanides(III) (5–7, 11); the uptake of these metal ions by RCSP decreases with decreasing pH. Figure 4 shows the uptake from strongly acidic media as well as the effect of acid species on the uptake. For all the acids tested, the uptake gradually decreases with increasing concentrations of the acids. Although marked differences were not observed in the uptakes from HCl, HNO_3, and H_2SO_4 media, H_3PO_3 significantly lowers the uptake. As is well known, Mo(VI) binds to H_3PO_4, forming bulky hetropoly acids, e.g., $H_3PMo_{12}O_{40}{\cdot}nH_2O$ (19). This complexing reaction actively competes with Mo(VI) uptake by the resins and/or makes the rapid diffusion of Mo(VI) into the resin phases difficult, resulting in a lowered Mo(VI) uptake. From Figs. 3 and 4 it can be concluded that a maximum capacity as high as ca. 3 mmol/g is observed around pH 1, except for H_3PO_4 media.

Next, the uptake from the low concentration level of Mo(VI) (0.0001 M) was examined in order to clarify its distribution behavior. Even from the low concentration level of 0.0001 M, RCSP took up more than 95%

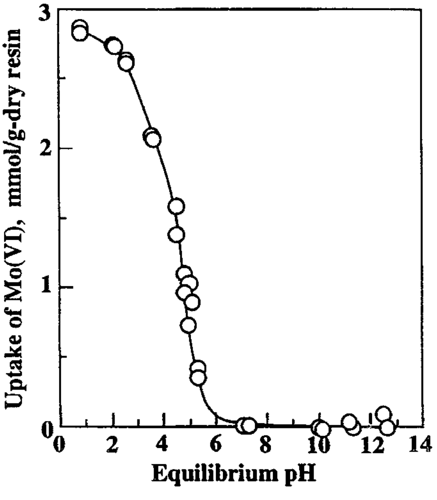

FIG. 3 The relationship between molybdenum(VI) uptake with RCSP and equilibrium pH of solutions.

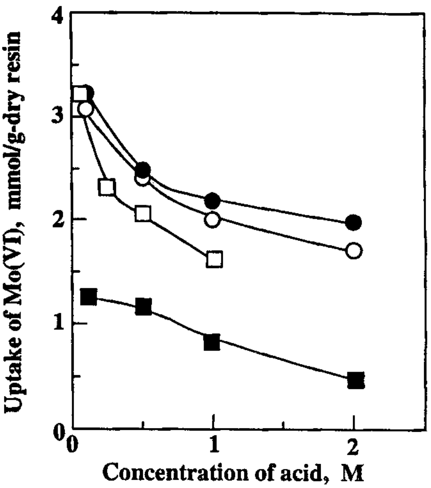

FIG. 4 Effect of acid concentrations and acid species on uptake of molybdenum(VI): (○) HCl, (●) HNO_3, (□) H_2SO_4, (■) H_3PO_4.

of Mo(VI) from pH 1 to 3. The relationship between log *D* and pH is shown in Fig. 5; here, −log[HCl] is adopted as the pH in the region where pH is less than 1. A simple relationship is not observed between log *D* and pH. The pH profile of log *D* is somewhat different from that of the uptake from 0.01 M solutions (Figs. 3 and 4), since the maximum values of log *D* locate around pH 2–3. Thus, it is difficult to estimate the detailed mechanism for the adsorption of Mo(VI) from the results presented. However, the pH profile of log *D* is very close to the one observed in extraction with organophosphonic acids (1, 2). This indicates that RCSP may also take up Mo(VI) through a mechanism similar to that proposed for the extraction of Mo(VI) with organophosphonic acids (1, 4).

Elution of Mo(VI) Adsorbed on RCSP

As already mentioned, Mo(VI) adsorbed on RCSP can be easily eluted with 1 M NaOH. However, elution with 1 M NaOH makes the subsequent elution of some metal ions, in particular, uranyl ion, difficult. We have already confirmed that the quantitative elution of uranyl ion from the RCSP column with aqueous Na_2CO_3 or HCl was extremely difficult to achieve, once the column had been contacted with 1 M NaOH (20), probably because uranyl ion is changed into its sparingly soluble hydroxides in

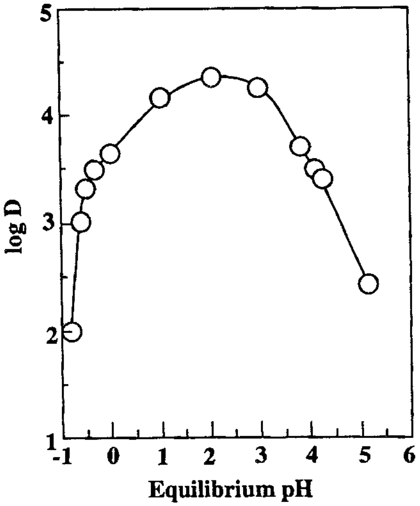

FIG. 5 The relationship between log *D* and equilibrium pH.

the resin particles. Consequently, we searched for an alternative eluting reagent which does not interfere with the subsequent elution of other metal ions.

From Fig. 3 it is expected that neutral and weakly basic electrolytes can be used as eluting reagents of Mo(VI), so elution with NaCl and CH_3COONa was tested. The results are summarized in Table 2, which clearly indicates that CH_3COONa can effectively elute Mo(VI). Quantitative elution with NaCl solutions is difficult to achieve. The high elution

TABLE 2
Elution of Mo(VI) with Sodium Acetate and Sodium Chloride Solutions

Concentration,[b] (M)	NaCl (mmol), 1.42[a]	CH_3COONa (mmol), 1.39[a]
0.1	0.36 (25)[c]	1.28 (92)
0.5	0.35 (25)	0.08 (6)
1	0.20 (14)	0.01 (1)
Total	0.91 (64)	1.37 (99)

[a] Amounts of Mo loaded to the RCSP column (resin 2 mL).

[b] 0.1, 0.5, and 1 M solutions were successively used, and the volume of each solution was 40 mL.

[c] Numbers in parentheses denote percentages of eluted Mo.

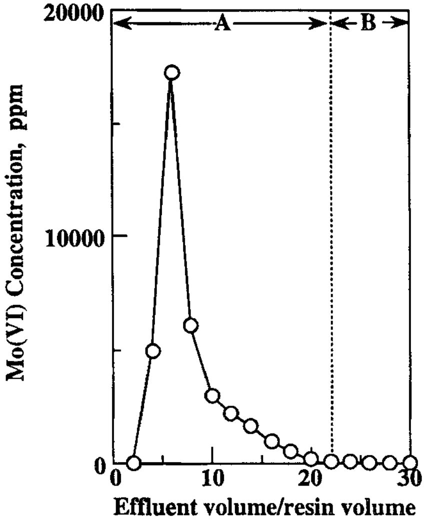

FIG. 6 Elution of molybdenum(VI) adsorbed on RCSP with 0.5 M sodium acetate. (A) 0.5 M CH_3COONa. (B) Water.

efficiency of CH_3COONa can be ascribed to the fact that acetate ion is a weak base.

Next, elution with 0.5 M CH_3COONa only was examined. After Mo(VI) was loaded to the 2 mL RCSP column (1.45 mmol), 0.5 M CH_3COONa was supplied to the column at an hourly rate of 10 bed volumes. The results are shown in Fig. 6. Although minor tailing is observed, Mo(VI) is quantitatively recovered with 20 bed volumes of 0.5 M CH_3COONa, and the highest concentration of Mo(VI) in the elution curve reaches 17 g/L.

The elimination of Mo from U is very important since Mo causes a serious problem even in trace amounts in uranium circuits. At present, Mo is eliminated from U by the solvent extraction techniques. The separation process of Mo(VI) based on the RCSP column operations will be useful for the separation of Mo from other metals including U. Indeed, our preliminary work for the separation of Mo from U gave promising results.

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