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ADSORPTION CHARACTERISTICS AND REMOVAL OF OXO-ANIONS OF ARSENIC AND SELENIUM ON THE POROUS POLYMERS LOADED WITH MONOCLINIC HYDROUS ZIRCONIUM OXIDE

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ADSORPTION CHARACTERISTICS AND REMOVAL OF OXO-ANIONS OF ARSENIC AND SELENIUM ON THE POROUS POLYMERS LOADED WITH MONOCLINIC HYDROUS ZIRCONIUM OXIDE

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ABSTRACT

Adsorption properties for oxoanions of Se(IV), Se(VI), As(III), As(V), and methyl derivatives of As(V) have been examined by the porous polymer beads loaded with monoclinic hydrous zirconium oxide (Zr-resin). The retention of these ions on the Zr-resin has been analyzed using Langmuir model of adsorption. The equilibrium constants and the capacities for above ions have been determined. The equilibrium constants for monomethyl arsinic acid and dimethyl arsinic acid are similar to that of As(V) but the adsorption capacity depends on the number of methyl groups. As(V) and Se(IV) are effectively retained on the Zr-resin from an aqueous solution of acidic to neutral pH region, whereas As(III) is removed from neutral to alkaline solution. The column system packed with

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the present Zr-resin can quantitatively remove low levels of As(V) and Se(IV) from aqueous solution.

Key Words: Separation; Oxoanions; Selenium; Arsenic; Zirconium oxide; Water treatment.

INTRODUCTION

Arsenic, selenium, and their compounds are extremely toxic, which potentially poses a particular hazard to the health and environment (1,2). Therefore, efficient separation of trace amounts of these compounds has become of increasing importance. Column process with solid adsorbent has a number of advantages in the separation and concentration of trace amounts of harmful materials from large quantities of water due to the high enrichment efficiency, ease in phase separation, and being free from additional chemicals (3,4). However, compared to the numerous studies of adsorbents for heavy metal cations, those of highly specific to oxo-anionic species are scarce (5–8). Moreover, because arsenic and selenium form various anionic species in aqueous solution by changing the oxidation state and organometallation due to microbial activities, their chemistry and speciation are not simple (9,10).

In our previous papers, we have incorporated crystals of hydrous zirconium oxide into the pores of a porous polymer resin (11–13). Because the resulting resin is porous and spherical in shape, it offers a great advantage for practical use in the separation and concentration process. In addition, zirconium is a rather harmless element, and its oxide has resistance against the attack of acids and alkalis. We found that hydrous zirconium oxide loaded resin (Zr-resin) is effective for selective adsorption of As(III) (H_3AsO_3) and As(V) (H_3AsO_4) as well as fluoride ions (11–13). In the course of our study, we noticed that hydrous zirconium oxide commonly retains various other oxo metal anions, especially those that can form weak conjugate acids. In the present work, we examined the adsorption characteristics of the Zr-resin for various arsenic and selenium compounds including methyl derivatives of As(V), As(V), Se(IV), and Se(VI). This paper also deals with the performance of Zr-resin with respect to adsorption selectivity, percent extraction, and applications to the separation and enrichment of arsenic and selenium compounds.

EXPERIMENTAL

Materials

The Zr-loaded resin (Zr-resin) was prepared by incorporation of $ZrOCl_2 \cdot 8H_2O$ into porous cross-linked polyacylate resin (Amberlite XAD-7,

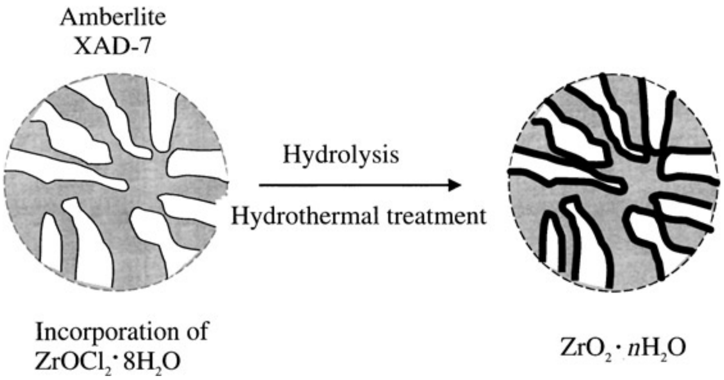

Figure 1. Preparative scheme of the Zr-resin. The resin matrix is Amberlite XAD-7 based on cross-linked polyacrylate copolymer.

Rohm & Haas Co., 32–60 mesh) followed by hydrolysis of the salt to give the hydroxide and hydrothermal treatment of the zirconium hydroxide (11,12). Figure 1 illustrates the preparative scheme of the Zr-resin. Hydrothermal treatment of zirconium hydroxide incorporated in the resin pores under acidic condition uniquely gave monoclinic hydrous zirconium oxide. The zirconium content in the resin is around 20%, which corresponds to 2 mmol of zirconium in the resin.

Adsorption Isotherm Experiments

Samples containing a 0.5 g portion of Zr-resin, various concentration of target ion, and buffer solution were placed in a 50-mL glass bottle. An acetate buffer solution (7.5×10^{-2} M) was used to adjust the solution of As(V) and Se(IV) compounds at pH 4.5, and ammonia-ammonium chloride (7.5×10^{-2} M) was used to adjust the solution of As(III) at pH 8. The whole system was shaken for 6 days in a thermostated room at 25°C, and then the equilibrium pH and the amount of ion in the solution were determined. The Langmuir constants were calculated according to the Langmuir isotherm equation (*vide infra*).

Measurements

The metal ion concentration was determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES) SEIKO Model SPS-1200A. Most of the adsorption experiments were carried out according to the reported procedures (11–13). Acid base titration of monomethylarsinic acid and dimethylarsinic acid was carried out by potentiometry at 25.0°C in aqueous solution (14). Typically, 100 mL of aqueous solution containing methylarsinic acid (0.4 mmol), 0.1 *M* $NaClO_4$, was titrated with standardized NaOH solution. Nitrogen gas was bubbled into the solution during titration. The pH was measured with a glass electrode after each addition, and the pK_a values were calculated using the program PKAS (14).

RESULTS AND DISCUSSION

Proton Dissociation Constants of the Conjugate Acids

As(III), As(V), Se(IV), and Se(VI) are present as oxo-anions with acid characteristic in water. Proton dissociation constants (pKa) and the chemical forms of the conjugate acids are listed in Table 1. The pK_a values for the monomethyl and dimethyl derivatives of As(V) were determined by potentiometry in this work. The pK_{a1} values of As(V) compounds increase about two orders of magnitudes with increase number of methyl group. Anions of higher valent elements appear to give much stronger conjugate acids. For example, conjugate acid of Se(VI) is much stronger than that of Se(IV), being comparable to sulfuric acid.

Adsorption Characteristics of the Zr-resin

Figure 2 shows the percent extraction of As(III), As(V), Se(IV), and Se(VI) as a function of pH. The adsorption of As(III), As(V), and Se(IV) is effective in wide pH range whereas quantitative removal of Se(VI) seems rather difficult. Effective adsorption was not realized at pH higher than 10 for all the ions. Moreover, they are released from the Zr-resin by treating with 1 *M* sodium hydroxide solution. The influence of the coexisting anion toward As(III), As(V), and Se(IV) adsorption was examined. The presence of common anions including Cl^-, NO_3^-, $CH_3CO_2^-$, and SO_4^{2-} did not interfere with the adsorption of Se(IV) in the concentration range up to 100 times to that of the objective ions. Among the anions examined, $H_2PO_4^-$ and fluoride ions significantly interfere with the adsorption of As(V) and Se(IV) due to

Table 1. Conjugate Acids of Arsenic and Selenium Species and Their Acid Dissociation Constants

	Abbreviation	pK_{a_1}	pK_{a_2}	pK_{a_3}	Literature
H_3AsO_3	As(III)	9.10	—	—	(15)
H_3AsO_4	As(V)	2.24	6.96	11.50	(15)
$H_2AsO_3(CH_3)$	$CH_3As(V)$	4.08	8.74	—	This work
$HAsO_2(CH_3)_2$	$(CH_3)_2As(V)$	6.12	—	—	This work
H_2SeO_3	Se(IV)	2.27	7.78	—	(15)
H_3SeO_4	Se(VI)	−3.0	1.70	—	(15)

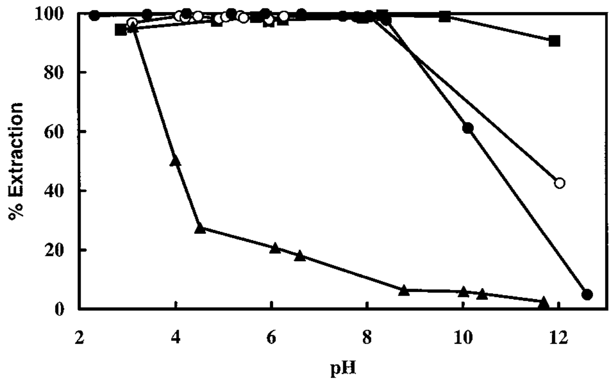

Figure 2. Percent extraction of oxo-anions by the Zr-resin as the function of pH. ● Se (IV), ▲ Se(VI), ■ As(III), ○ As(V). Resin: 0.5 g; [M] = 2 m*M*; shaken 6 days at 25°C.

a competing adsorption to zirconium. As given in Figure 3, the percent extraction values for As(V) and Se(IV) at pH 4.5 decreased to leach less than 40% in the presence of 100 times of phosphate or fluoride ion.

Many of the oxo-anions whose conjugate acids are weak have been retained more firmly to Zr-resin than the anions of strong acid such as NO_3^-, SO_4^{2-}, and SeO_4^{2-}. Thus, the origin of interaction between anions and zirconium cannot be interpreted simply by electrostatic force, or in other words ion-exchange mechanism.

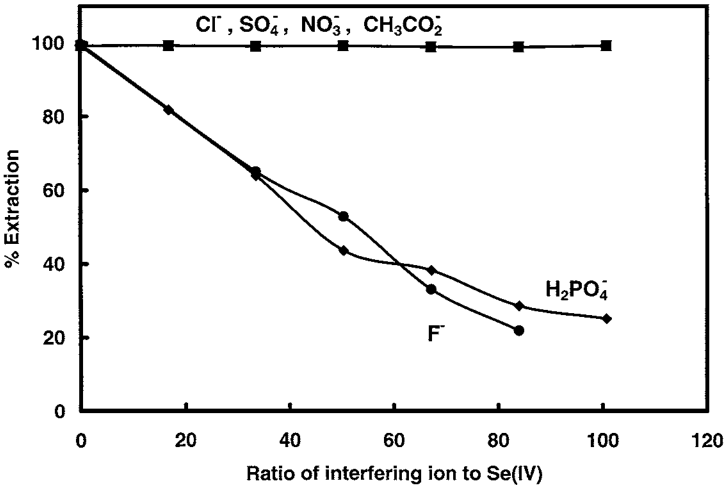

Figure 3. Effect of diverse ions on the percent extraction for the adsorption of Se(IV). Resin: 0.5 g.; [M] = 2 m*M*, pH 6.6; shaken 6 days at 25°C.

According to our preliminary work, $[Zr(H_2O)_2EDTA]$ as a model compound can form ternary complexes with a series of oxo-anions including As(III), As(V), and Se(IV) as given in the following equation (1), where MO_x denotes

$$[Zr(H_2O)_2EDTA] + MO_x = [Zr(MO_x)EDTA] + 2H_2O \qquad (1)$$

oxo-anions (16). The ligand exchange reaction with coordinated water is a plausible mechanism for the selective retention of the anions to the present resin. As mentioned above, oxo-anions are released from the resin when the Zr-resin is exposed in alkaline solution due to the replacement of anions with hydroxide ion. However, the resin performance at this stage is significantly low unless the resin is not treated with acidic solution. Rinsing the resin with acetate buffer of acidic pH is very important for regeneration and repeated use of the Zr-resin. Thus, protonation of hydroxyl groups on the zirconium to convert into aquo form is essentially required to retrieve the ligand exchange property.

Adsorption Isotherms

The adsorption characteristics of the monoclinic Zr-resin with respect to the equilibrium constant and adsorption capacity have been examined using the Langmuir model of adsorption (17). The following equation (2) was used to calculate the equilibrium constant (K) and the capacity of the adsorbent (C_s), where C is the concentration of the target ion in solution and C_x is that in the resin at equilibrium.

$$C/C_x = (1/KC_s) + (C/C_s) \qquad (2)$$

Plots of C/C_x against C for As(V) gave a good straight line for the adsorption of As(III), methylated As(V), and Se(IV). Figure 4 shows the typical plots for As(III), As(V), and Se(IV). From the intercept and slope we derived $\log K$ and C_s for these ions and the obtained values are listed in Table 2 along with those of methylated As(V). The $\log K$ values for all the As(V) species are similar to each other. However, the capacity values for As(V) species decrease with the increase of substituted methyl group presumably due to the increase of steric hindrance. Practically no adsorption took place for trimethylarsin in which the dissociative proton is absent.

Column Adsorption

Column adsorption of Se(IV) has been carried out with the present resin. Typically, a buffered solution containing 10 ppm of Se(IV) at pH 4.0 was continuously passed through the column packed with 5 g (11.8 mL, i.d. 1.1 × 12 cm) of the

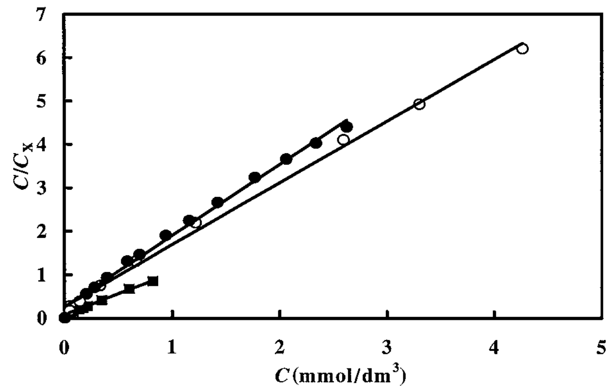

Figure 4. Langmuir plot for the adsorption of ■ As(III), ○ As(V), and ● Se(IV) by the Zr-resin. Zr-resin: 0.5 g; temperature: 25°C.

Zr-resin at a rate of 1 mL/min. The solution out of the column was fractionated, and the concentration of Se(IV) was monitored not to exceed the permission limit of Japanese industrial standard (i.e., 0.1 ppm). Figure 5 shows the typical column breakthrough profile for Se(IV). The Se(IV) was favorably retained on the column to allow the passage of the feed solution for more than 500 times the bed volume. The presence of 1000 ppm each of nitrate, chloride, and sulfate did not interfere with the adsorption of Se(IV) (10 ppm) in a similar column experiment. The Se(IV) retained on the column was released from the resin by elution with 1 *M* NaOH. The column was used repeatedly on washing with water, rising with 0.2 *M* acetate buffer of pH 4.2 followed by washing with water. The column performance has been kept in the second adsorption cycle as given in Figure 5. In a similar manner, As(V) and As(III) were also favorably retained on the column at pH 5 and 9, respectively. More than 99% of the adsorbed ions were released by elution with less than 70 mL of 1 *M* NaOH. Leaking of zirconium was practically negligible during the adsorption, desorption, and regeneration cycles.

Table 2. Langmuir Constants for the Adsorption of Various Oxo-Anions (25°C)

	pH_{eq}	C_s (mmol/g)	log K
As(III)	8.5	1.06	4.05
As(V)	4.5	0.72	3.65
CH_3-As(V)	4.5	0.61	3.85
$(CH_3)_2$As(V)	4.5	0.19	3.27
Se(IV)	4.5	0.49	4.21

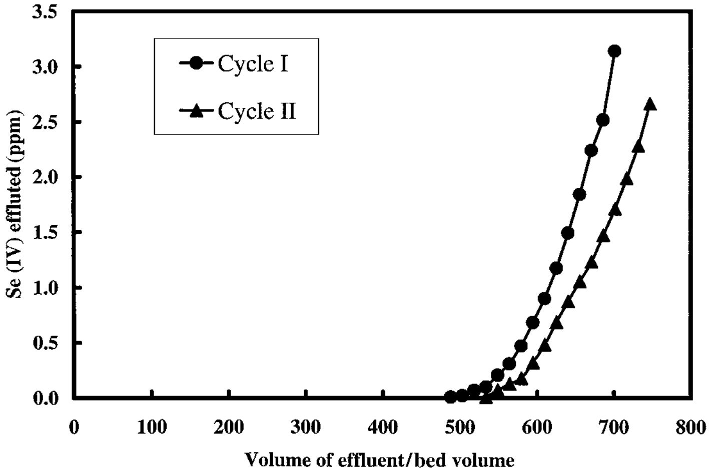

Figure 5. Column breakthrough profile for the adsorption of Se(IV) for first (●) and second (▲) runs after regeneration. By the Zr-resin. Se(IV) feed: 10 ppm, pH 4.0; flow rate = 1 mL/min; volume of fraction = 18.3 mL.

Removal of As(V) Spiked in Tap Water

An attempt was made to remove As(V) spiked in tap water in order to apply the resin for the practical use. The anions existing in the tap water were mainly chloride ions, whose content was less than 100 ppm. Tap water spiked with 1 ppm of As(V) was continuously passed through the column (15 ml resin bed) at a flow rate of 2.5 mL/min (SV = 10). Concentration of As(V) and zirconium in the solution out of the column as well as pH were monitored at appropriate time intervals, and the results are listed in Table 3. The leaking of As(V) was less than

Table 3. Continuous Column Adsorption Test of As(V) Spiked in Tap Water

Days	pH of Outlet	As Found (ppb)	Zr Leaked (ppb)
1	5.2	4.9	—
7	6.1	1.7	—
14	6.1	0.8	—
18	5.9	1.8	6
21	5.5	4.9	3
28	5.6	46.3	—

Zr-resin: 15 mL; feed solution: As(V) = 1 ppm; flow rate: 2.5 mL/min (SV = 10).

Japanese standard allowance of drinking water (>0.01 ppm) until at least 21 days. Leaking of zirconium was practically negligible during this operation. This verifies that the present Zr-resin is promising for the removal of low concentrations of As(V) from actual tap water.

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