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Selective Separation of Arsenic(III) and (V) Ions with Ferric Complex of Chelating Ion-Exchange Resin *

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Abstract

Trace levels of aqueous arsenic(III) and (V) ions were adsorbed selectively onto the ferric complex of a chelating resin, Uniselec UR-10. The adsorption was markedly dependent upon the pH of the aqueous phase. The distribution ratio and the specific adsorption capacity of arsenic(III) were 23,000 and 0.47 mmole/g, respectively, at the optimum pH for the adsorption, 9.2. The corresponding values of arsenic(V) were 22,000 and 0.53 mmole/g at the optimum pH 5.5. In the column operation the adsorption of the arsenic ions was also dependent upon the flow velocity and the size of the resin particle. A velocity of 60 cm/hr and 100 to 200 mesh size afforded satisfactory results. Adsorbed arsenic was recovered quantitatively by eluting the resin with 2 *N* hydrochloric acid, where the complexed iron was also eluted. A trace level of arsenic in wastewater from a geothermal power plant was successfully separated in the presence of a large excess of diverse cations and anions. Trace arsenic in natural seawater was also successfully preconcentrated 100 to 200 times over the

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original level by adsorption onto the ferric resin followed by elution with hydrochloric acid.

The adsorption of trace anions in an aqueous solution has been studied by use of various hydrous metal oxides (*1*). Ferric hydroxide was known to adsorb the oxo anions of arsenic(III) and (V) in preference to other diverse anions (*2–4*). We also reported previously on the adsorption of arsenic(III) and (V) ions by ferric hydroxide loaded on silica gel particles (*5*). The gel particles which could retain iron(III) up to 3.3% on a dry weight base adsorbed about 0.07 mmole of arsenic per 1 g of the dry ferric gel at pH 6. Since the adsorption capacity increased with an increase of iron content in the gel, the adsorption site for arsenic ion was obviously the ferric ion on the gel surface. As an extention of this investigation, we attempted to increase the effective iron content on a solid support by the use of a chelating resin, Uniselec UR–10, in place of silica gel. The UR–10 resin has a three-dimensional network structure containing an *o*-hydroxybenzylnitrilodiacetic acid moiety as a chelating group, which forms very stable chelates with various heavy metal ions and is capable of retaining iron(III) threefold over silica gel. Furthermore, the chelating resin has an advantage over the ordinary cation exchange resin because iron(III) is so tightly bound to the resin through coordination bonds that it is not easily released from the resin even in the presence of a large excess of alkali or alkaline earth cations at above pH 3. The adsorption behavior of arsenic ions with the ferric complex of the chelating resin was investigated to explore the possibility of this method as a separation process of arsenic ions in environmental or wastewater, as well as to evaluate this process as a preconcentration technique for trace levels of arsenic in aqueous samples.

EXPERIMENTAL

Materials

Uniselec UR–10 chelating resin (Unitika Ltd., Osaka, Japan) of two different sizes, 100–200 mesh (finer) and 20–50 mesh (coarser), was used. The resin was supplied as the sodium salt form immersed in water. About 100 g of the wet sodium form resin was washed with three 300 ml portions of 2 *M* sodium hydroxide and 2 *M* hydrochloric acid, alternatively, and finally equilibrated with 2 *M* sodium hydroxide. After it had been sucked off from the mother liquor, the resulting sodium form resin was packed into a chromatographic tube of 3 cm i.d. Then the resin was washed with 500 ml of deionized water, followed by elution with 2000 ml of 0.05 *M* ferric chloride at a flow rate of 100 ml/hr. The ferric chloride solution was adjusted to pH 3.5 with acetate buffer. The resulting ferric chelating resin was again washed with deionized watei until the eluate washings became free from ferric ion, sucked off, and stored in a sealed bottle in a refrigerator.

The iron contents in the ferric resin thus obtained were 10.3 wt-% or 1.84 mmole/g for the finer resin, and 9.06 wt-% or 1.62 mmole/g for the coarser resin, based on the dry, free acid resin. The sucked ferric resin of the finer and coarser sizes retained water of 89 and 127 wt-%, respectively.

Stock solutions of arsenic(III) and (V) were prepared from arsenic trioxide and sodium arsenate heptahydrate, respectively. The sample solutions for adsorption experiments were prepared by diluting an aliquot of the stock solution with deionized water, with or without the buffer solution in most cases, and in some cases with the wastewater from a geothermal power plant at the side of Mt. Kujyu. The analytical data on the representative sample are listed in Table 1. Seawater was sampled at the northern coast of Shikanoshima island near Fukuoka.

Acetic acid–sodium acetate buffer and ammonium chloride–ammonium hydroxide buffer were employed to adjust the pH of the sample solution in the ranges of 3 to 6 and 7 to 10, respectively. All other reagents were of analytical grade.

Iron was determined by the atomic absorption method, and arsenic was determined by the spectrophotometric method based on color development with silver diethyldithiocarbamate (*7*).

TABLE 1

Analytical Result on Wastewater from Kujyu Geothermal Power Plant (*6*)

Ion	Concentration (ppm)	Ion	Concentration (ppm)	Ion	Concentration (ppm)
F^-	3.8–5.0	$H_2PO_4^-$	0.02	Li^+	4.5–13.2
Cl^-	1220–2330	HPO_4^{2-}	0.8–2.1	K^+	105–289
Br^-	2.5–6.3	BO_2^-	9.8–10.6	Na^+	805–1396
I^-	0.2–0.5	$HSiO_3^-$	23.0–38.9	Ca^{2+}	9.9–19.8
SO_4^{2-}	98–214	OH^-	0.04	Mg^{2+}	0.01–0.19
HCO_3^-	46–76	SiO_3^{2-}	0.01	Fe^{2+}	0.03–0.06
CO_3^{2-}	1.4–2.1	As	1.53	Al^{3+}	0.02–0.09

Procedure for Adsorption Study

Batchwise Operation. A weighed amount of the ferric resin was shaken with 50 ml of a buffered arsenic solution for a specified period of time, or until the adsorption attained equilibrium at 30 °C, whereupon the ionic strength was adjusted to 0.1 with potassium chloride. After removing the resin from the solution, determination was made for arsenic remaining in the solution, while the arsenic adsorbed on the resin was determined on the extract with 2 *M* hydrochloric acid from the resin phase. The specific adsorption capacity of the ferric resin, C_{ad}, was calculated in terms of mmole of adsorbed arsenic per 1 g of dry ferric resin.

Column-type Operation. A glass tubing of 0.61 cm i.d. was packed with 4.0 g of sucked ferric resin to give a column of 4.6 ml in volume and 15.7 cm high. A sample solution adjusted at a certain pH was passed through the column at room temperature (about 30 °C). The effluent was collected in 15 ml fractions and each was analyzed for arsenic. The ferric ion concentration and pH of each fraction were also measured.

Preconcentration of Arsenic Ion in Seawater by the Column-type Operation

A certain amount of seawater (10 to 20 liters) was passed at room temperature (about 30 °C) at a flow velocity of 40 cm/hr through a column of the finer ferric resin which was packed in 1.05-cm i.d. tubing of 11.5 cm height and 10 ml volume. Then the adsorbed arsenic ion was eluted with 80 ml of 2 *M* hydrochloric acid. The eluate was diluted in a volumetric flask and a 10 or 20 ml aliquot was analyzed for arsenic.

Instruments

A Toa model HM-10B was used for pH measurements. Arsenic and iron were determined on a Hitachi 200 spectrophotometer and Jarrel-Ash AA-1 spectrophotometer, respectively.

RESULTS AND DISCUSSION

Batchwise Operation

Figures 1(a) and 1(b) show the rate of adsorption of arsenic(III) and (V) onto the ferric resin in the batchwise operation in terms of the fractional

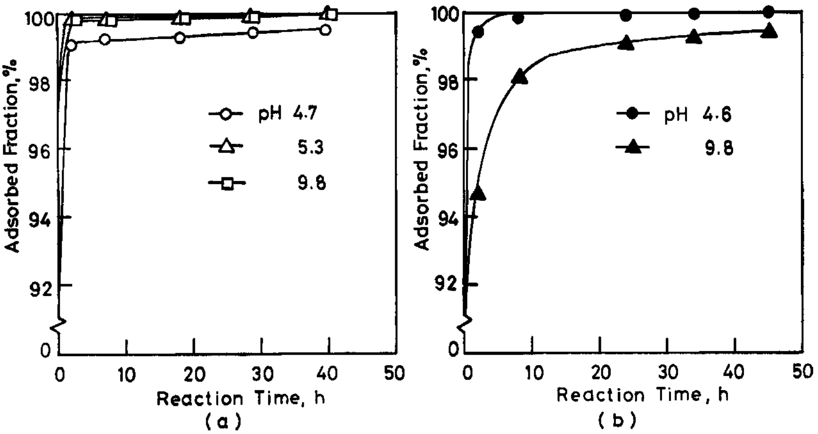

FIG. 1. The rate of adsorption of arsenic onto the ferric resin at 30°C. (a) As(III). (b) As(V).

ratio of the initial amount of arsenic ion present in the sample solution. When the pH of the solution was 5.3 to 9.8, arsenic(III) ion was adsorbed completely within 2 hr, a lower pH such as 4.7 causing less efficient adsorption, e.g., 98% even after 40 hr. Adsorption of arsenic(V) ion proceeded in the reverse manner, rapidly at pH 4.6 but very slowly at a higher pH such as 9.8. Although the adsorption capacity was not definitely confirmed because it varied with the pH of the aqueous phase (as will be described below), the adsorbent was always present in a large excess compared to the amount of arsenic ion to be adsorbed, which was chosen as 0.067 mmole in each experiment. These results indicated that it might require more than 60 hr to attain adsorption equilibrium at 30°C.

Figure 2 shows the pH profile of partition ratio, K_{ad}, which is defined as

$$K_{ad} = [As]_{ad}/[As]_{aq}$$

where $[As]_{ad}$ is the mole of arsenic adsorbed onto a unit weight of the dry ferric resin and $[As]_{aq}$ is the molar concentration of arsenic ion in an aqueous phase in adsorption equilibrium. Adsorption of arsenic(III) was the most favored in the vicinity of pH 9, where K_{ad} was 23,000. For arsenic(V), on the other hand, pH 5.5 afforded the optimum adsorption, where K_{ad} was 22,000. K_{ad} of both arsenic ions decreased rapidly as the pH varied on either side of the optimum value. Such a pH profile of the adsorption suggests that the arsenite and arsenate univalent anions $H_2AsO_3^-$ and $H_2AsO_4^-$ are responsible for adsorption if one refers to

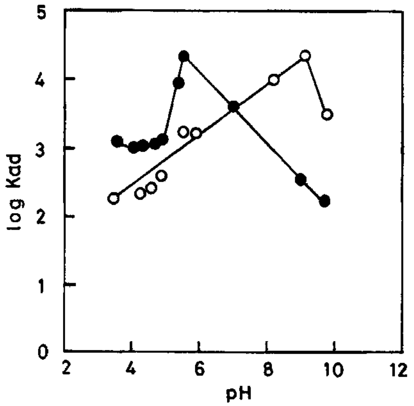

FIG. 2. The pH profiles of log K_{ad} of arsenic at 30 °C. $\mu = 0.1$ with KCl. (○) As(III); (●) As(V).

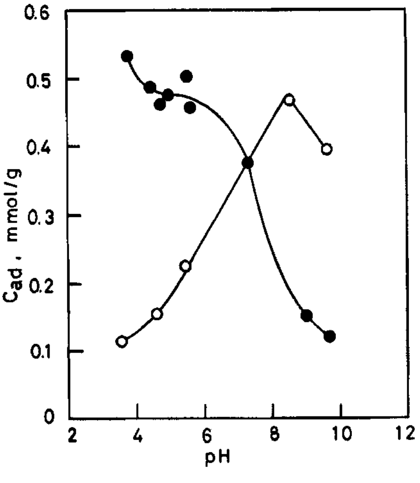

FIG. 3. The pH profiles of the specific adsorption capacities, C_{ad}, at 30 °C. $\mu = 0.1$ with KCl. (○) As(III); (●) As(V).

the values of acid dissociation constants of both acids ($pK_1 = 9.2, pK_2 = 12.1$, and $pK_3 = 13.4$ for H_3AsO_3, and $pK_1 = 2.2, pK_2 = 6.9$, and $pK_3 = 11.5$ for H_3AsO_4) (*8*).

As the functional group of the chelating resin, "UR-10," is a quadridentate *o*-hydroxybenzylnitrilodiacetic acid, the hexacoordinate ferric ion may be bound to the resin under so-called "coordination unsaturated" state, leaving two coordination sites aquated. Although the nature of adsorption of arsenic ion to the ferric resin is not yet fully elucidated, it is very likely that the adsorption of arsenic ion may occur on the unoccupied coordination sites of the resin-bound ferric ion (*9*).

Adsorption modes of both anions are of a typical Freundlich isothermal nature in the same manner as the silica gel loaded with ferric hydroxide (*5*), suggesting that the arsenic ions adsorb onto ferric ion with a wide spectral band of the adsorption energy.

Figure 3 shows the pH profile of the specific adsorption capacities, C_{ad}, of the ferric resin for arsenic(III) and (V) ions. The C_{ad} for arsenic(III) shows a maximum value of 0.47 mmole/g at pH 8.5, while arsenic(V) shows a larger C_{ad} value (0.47 to 0.53 mmole/g) at a lower pH region (3.6 to 5.5). The parallelism between C_{ad} and K_{ad} is indicative that arsenite and arsenate univalent anions play the major roles in adsorption.

Column-type Operation

Figure 4 shows the results of adsorption of arsenic(III) on a column of the ferric resin. A sample solution which contained arsenic(III) at about 100 ppm and was buffered at pH 8.1 was passed at a velocity of 52 to 113 cm/hr. At a flow velocity of 52 cm/hr, 700 ml of the effluent was passed up to the breakthrough point, and 930 ml was passed up to the half-height point of the sigmoidal breakthrough curve. C_{ad} was calculated from the breakthrough curve to be about 0.56 mmole/g, which was slightly higher than that obtained from the batchwise operation. The higher flow velocity caused the earlier breakthrough of arsenic, and the optimum velocity on the finer resin column is likely to be at about 60 cm/hr.

Figure 5 shows the breakthrough curve of arsenic(V), where the initial arsenic level was at about 100 ppm and pH was adjusted to 8.4, which is close to that observed for wastewater from a geothermal power plant, although it is not the optimum pH for the adsorption of arsenic(V). The breakthrough occurred when 325 ml of the effluent was passed, and the effluent volume up to the half-height point was 410 ml. The C_{ad} was

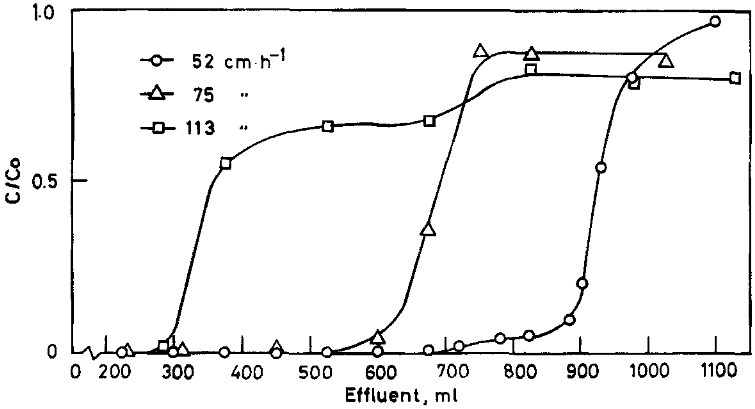

FIG. 4. The break-through curves of arsenic(III) ion at room temperature ($\simeq$30 °C). The initial arsenic concentration, C_0, of the influent solution was about 100 ppm, and the solutions were buffered at pH 8.1 with 0.02 *M* NH_4Cl–NH_4OH.

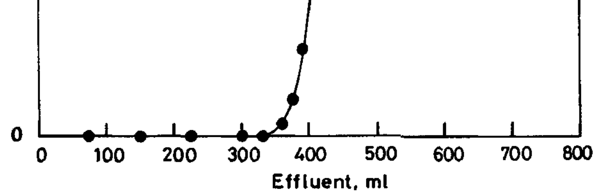

FIG. 5. The breakthrough curve of arsenic(V) ion at room temperature ($\simeq$30 °C). C_0 was about 100 ppm, and the solution was buffered at pH 8.4 with 0.02 *M* NH_4Cl–NH_4OH.

calculated from the curve to be 0.24 mmole/g, in good agreement with that obtained from batchwise operation.

Figure 6 shows the adsorption curves of arsenic(III) and (V) obtained on model experiments by the use of wastewater from a geothermal power plant in which the original concentration of arsenic was about 2 ppm and the pH was 8.4 as shown in Table 1. In the experiments, arsenic(III) and (V) were added to the wastewater so that the arsenic level was elevated to about 100 ppm and resulting solutions were of pH 7.8 to 7.9. With the use of such wastewater, the breakthrough of arsenic(III) was observed when 125 to 150 ml of the effluent had been passed, and the elution volume up to the half-height point on the breakthrough curve was 220 to 250 ml, where the flow velocity was chosen at 22 to 48 cm/hr. The C_{ad} was calculated from Curves I and II to be 0.14 to 0.10 mmole/g, which was approximately one-third to one-fourth of those obtained for batchwise operation. This decreased C_{ad} is due to the lowered pH (3.8 to 4.8) in the eluates, which makes them unfavorable for adsorption of arsenic(III). The addition of a small amount of 2 *M* ammonium hydroxide to the influent caused the elevation of the initial pH to 9.7, and results in the increase of C_{ad} to 0.23 mmole/g, which was calculated from Curve III. When the solution was buffered at pH 8.5, C_{ad} was further elevated as high as those obtained in Fig. 4. As to the C_{ad} for arsenic(V), a value of 0.38 mmole/g was

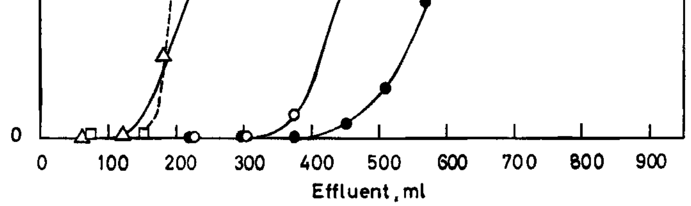

FIG. 6. The breakthrough curves of arsenic(III) and (V) ions in the wastewater from a geothermal power plant. The pH of the solution was about 7.8, and C_0 was elevated to about 100 ppm with the addition of arsenic solution. (○) As(III); (●) As(V). Curve I: As(III), 22 cm/hr. Curve II: As(III), 48 cm/hr. Curve III: As(III), 49 cm/hr, pH of influent solution was elevated to 9.7 with the addition of NH_4OH. Curve IV: As(V), 27 cm/hr.

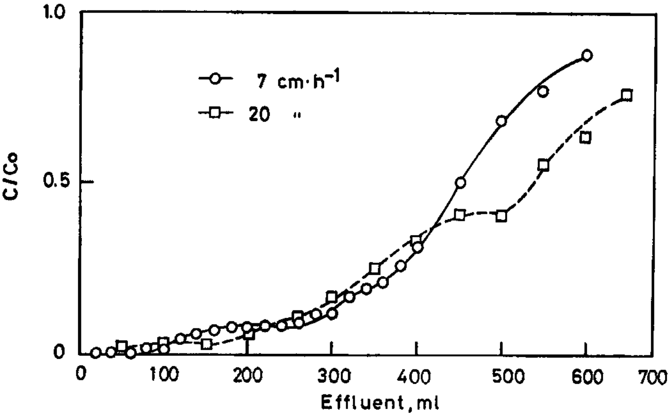

FIG. 7. The breakthrough curves of arsenic(III) ion at room temperature ($\simeq$30 °C) on a column of the coarse ferric resin. pH $\simeq$ 9.8 with 0.02 *M* NH_4Cl–NH_4OH; $C_0 \simeq 100$ ppm.

calculated from Curve IV, where the lowered pH in the eluate favored the adsorption of arsenic(V), as is clearly shown in Fig. 3. The decrease in pH of the eluate on passing through the column of ferric resin may be explained by the proton dissociation of coordinated water on ferric ion in the resin, if one refers to the ionization constant of the ferric aquo ion (*8*):

$$Fe(OH_2)_6^{3+} \rightleftarrows Fe(OH_2)_5(OH)^{2+} + H^+, \qquad pK_a = 2.3$$

When wastewater of pH 8.4 or 0.1 *M* potassium chloride of pH 7.1 was passed through a column of the ferric resin, the pH of the first portion of effluent was decreased to 3.8. It gradually increased to 4.5 as elution was continued, but never exceeded 5. Elution of a buffered solution at pH 8.2 also gave an eluate with a lowered pH in the first fraction, but it recovered rapidly to the originally buffered pH.

Figure 7 shows the adsorption curves of the arsenic(III) obtained on a column packed with 4.6 ml of the coarser ferric resin. Adsorption did not reach saturation within the observed period at this temperature, even at a velocity as slow as 7 cm/hr. The early breakthrough of arsenic and the late saturation of the columned resin indicate that the ferric resin of coarser size is a poor adsorbent in this condition.

TABLE 2

Log K_{ad} Values in 2 *M* Alkaline Solutions

2 *M* Alkaline solution	$[OH^-]$	log K_{ad}	
		As(III)	As(V)
NaOH	2	1.75	1.81
Na_2CO_3	2×10^{-2}	2.46	1.92
NH_4OH	6×10^{-3}	2.44	1.85
CH_3COONa	3.4×10^{-5}	3.47	3.49

Recovery of Arsenic

In principle, the adsorbed arsenic may be desorbed in two ways. One is to strip arsenic from the ferric resin by an alkaline eluent, and the other is to desorb arsenic together with ferric ion by an acid eluent. In the former case the ferric complex of chelating resin can be recovered intact and might be recycled as the adsorbent. For this purpose, one might expect from the pH profile of K_{ad} (Fig. 2) that concentrated aqueous alkali would be useful as a desorbing agent for arsenic. However, log K_{ad} of arsenic ions in various alkali, as summarized in Table 2, is approximately 1.8 or above, indicating that an appreciable amount of arsenic still remains adsorbed onto the ferric resin even in the presence of a large excess of competing anionic ligands, and that the alkaline stripping method is practically of no use.

On the other hand, arsenic retained on the ferric resin could be recovered quantitatively with 5 to 10 times the column bed volume of 2 *M* hydrochloric acid. In this case, iron was also dissolved into the effluent together with arsenic, and consequently it is necessary to convert the resin to the ferric complex in advance of the next adsorption cycle.

Preconcentration of Arsenic in Seawater

Another useful application of ferric resin was in the preconcentration of arsenic in natural seawater. By adsorption onto the columned ferric resin followed by elution with 2 *M* hydrochloric acid, arsenic in the eluate was concentrated 100 to 200 times that in the seawater. Arsenic concentration in the sample of seawater was determined to be 1.65 ± 0.13 ppb, in accord with the average levels of 1.65 ppb at Sugashima in Japan *(10)* and 2.0 ± 0.026 ppb in Great Britain (*11*). This method is a useful technique of the preconcentration of a trace level of arsenic ions in aqueous solutions in general.

Acknowledgments

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