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Selective Adsorption of Arsenic(V) Ion by Use of Iron(III) Hydroxide-Loaded Coral Limestone

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Abstract

By use of iron(III) hydroxide-loaded coral limestone (abbreviated Fe-coral) as an adsorbent, a trace level of arsenic(V) ion in aqueous solution could be efficiently and selectively adsorbed onto the adsorbent surface. The arsenic adsorptibility of the Fe-coral depended upon the amount of iron(III) hydroxide loaded on the coral limestone. The arsenic adsorption was almost unaffected by the initial pH of the solution in the pH range 2–10, and was not practically influenced by the addition of such anions as chloride, nitrate, sulfate, perchlorate, and acetate in the aqueous solution. However, only coexisting phosphate caused a great depression in the arsenic adsorption. The arsenic absorbed onto Fe-coral was hardly desorbed in contact with an aqueous solution under a wide pH range (3.5–10). The arsenic adsorption was effectively applied to a column-type operation.

INTRODUCTION

In Japan, the arsenic level of water is regulated below 0.5 ppm in wastewater and 0.05 ppm in natural water. Accordingly, a water-treatment process is necessary to remove arsenic from industrial wastes in order to reduce its arsenic content below the regulation values.

The most common method used for the removal of arsenic from an aqueous phase is precipitation with lime and iron(III) salts followed by adsorption onto the resultant iron(III) hydroxide flocs (*1*). However, such flocs are usually fine and in colloidal form, so that it takes a long time to settle and filtrate the flocs. Moreover, it is difficult to dewater the flocs, leading to the production of a large volume of sludges.

Other arsenic-removal methods, adsorption on activated carbon (*2–4*), metal-loaded activated carbon (*5*), activated alumina (*6*), red mud (*7*), or iron-loaded chelating resin (*8*), have also been discussed. However, there still remain several problems such as disposal of the enormous volume of arsenic-adsorbed sludges and the high cost of treatment.

In the present work a rapid and effective method of arsenic adsorption is developed by use of iron(III) hydroxide-loaded coral-limestone (a porous limestone). Such an arsenic removal method is of great advantage over ordinary methods with respect both to solid–liquid separation and to cost.

EXPERIMENTAL

Preparation of Arsenic Adsorbent, Iron(III) Hydroxide-Loaded Coral Limestone

The coral limestone used was Porelime (Tokunoshima Coral Reef Co., Ltd., Japan), and its particle size was adjusted to 8–120 mesh. Then the coral particles were rinsed with water several times and dried in an electric oven (100°C).

The resultant coral particles (50 g), which were used as a support, were soaked in an aqueous solution (200 mL) containing 2 wt% iron(III) chloride for 1 day, then the iron(III) hydroxide-loaded particles were well-rinsed with water, dried (100°C), and sieved on 120 mesh to remove the free hydroxide particles, resulting in the preparation of Fe-coral.

Determination of the Iron Loaded on the Fe-Coral

The Fe-coral (1.0 g) prepared was completely dissolved into 3 M (1 M = 1 mol/dm^3) hydrochloric acid solution (20 mL), and the iron concentration in the solution was determined by atomic absorption spectrophotometry using a Nippon Jarrel Ash AA-855.

Arsenic Adsorption Procedure

Sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$, 0.416 g) was dissolved in 100 mL water, resulting in the preparation of 100 ppm of arsenic standard solution.

A 1.0-g of Fe-coral was shaken with an arsenic solution (20 mL) for 5 h at 25°C. After removing the Fe-coral, the concentration of arsenic remaining in the aqueous solution was determined by flameless atomic absorption spectrophotometry (AA-855 with a flameless atomizer unit FLA-1000).

Arsenic Desorption Procedure

An arsenic-adsorbed Fe-coral (21 μg arsenic was adsorbed on 1 g of dry Fe-coral) was allowed to shake with an aqueous solution (20 mL) which was adjusted at a certain pH. After removing the Fe-coral, the amount of arsenic desorbed from the Fe-coral into the aqueous phase was measured.

Column Operation

A glass tube of 29 mm i.d. was packed with 20 g Fe-coral to give a column 17 mL in volume and 25 mm high. An aqueous solution containing 1.0 ppm arsenic(V) was passed through the column at room temperature (~25°C) at a flow velocity of 100 mL/h. The effluent was collected in 7-mL fractions, and each was analyzed for arsenic.

RESULTS AND DISCUSSION

Figure 1 shows the adsorption of arsenic(V) (arsenate) onto the Fe-coral as a function of arsenate concentration in the aqueous solution. These adsorption isotherms were almost linear. Thus, the adsorption mode is of a typical Freundlich isothermal nature. As seen in Fig. 1, the Fe-coral exhibited much higher adsorptibility compared to unloaded coral.

Moreover, through the repetition of the procedure of iron(III) hydroxide loading, the iron amount loaded on the Fe-coral could be increased.

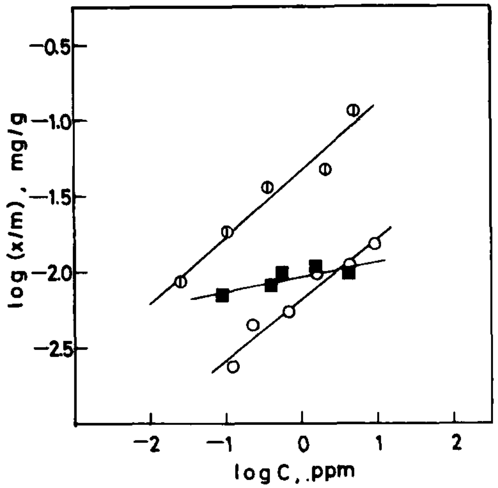

FIG. 1. Adsorption isotherm of arsenic(V) on various adsorbents (⦶: Fe-coral; O: unloaded coral; ■: Kansuiseki). *C* and *x*/*m* denote the equilibrium concentration of As(V) in solution and that in adsorbent, respectively.

Figure 2 indicates the adsorption isotherm of arsenic onto the multiloading Fe-coral. The arsenic adsorption was somewhat increased with an increase in the amount of iron (Fig. 3). These results suggest that the arsenic adsorption mostly occurs at the active sites of iron(III) hydroxide deposit on the Fe-coral.

When Kansuiseki (Nittofunka Kogyo Co., Ltd., Japan; calcite, $CaCO_3 >$ 99%) was used as a reference support of iron(III) hydroxide, the arsenic adsorption was greatly decreased (Fig. 1).

The adsorption mechanism is presumed as follows. When coral is soaked into aqueous iron(III) chloride solution, the following reaction occurs on the coral surface:

$$2Fe^{3+} + 3CaCO_3(coral) + 3H_2O \rightarrow 2Fe(OH)_3\downarrow + 3Ca^{2+} + 3CO_2\uparrow$$

The strongly acidic aquo-iron(III) complex immediately reacts with the calcium carbonate of the coral and generates colloidal iron(III) hydroxide with the evolution of carbon dioxide gas. The generated colloid is effectively and tightly deposited onto the porous coral surface, resulting in the preparation of Fe-coral.

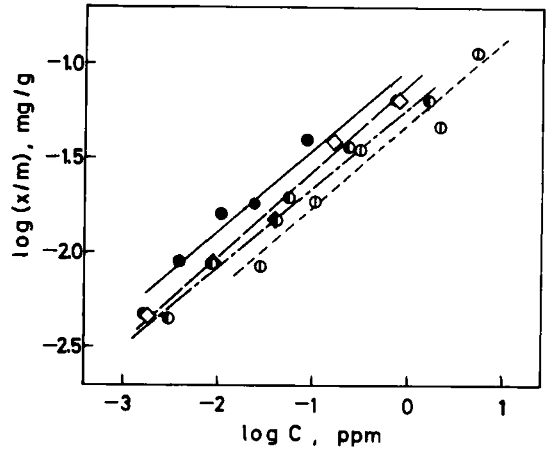

FIG. 2. Adsorption isotherm of arsenic(V) on multiloading Fe-coral. The iron(III) hydroxide loading treatment was carried out once (⦶), twice (◐), three times (◇), or four times (●). *C* and *x*/*m* denote the equilibrium concentration of As(V) in solution and that in adsorbent, respectively.

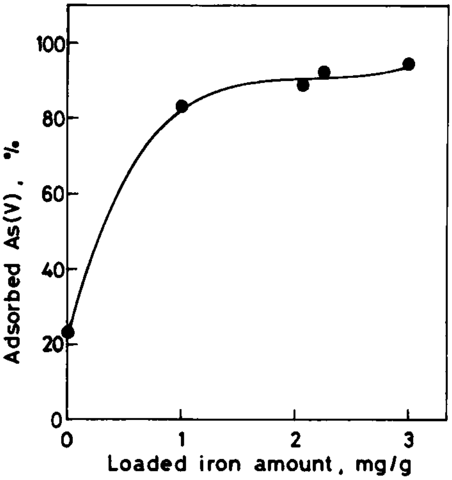

FIG. 3. Dependence of arsenic adsorption on the amount of loaded iron. The aqueous phase initially contained 2.0 ppm arsenic(V).

Although the nature of arsenic adsorption onto the iron(III) hydroxide surface has not been completely elucidated, it is very likely that the adsorption occurs via the ligand-exchange reaction of the hexacoordinate iron(III) ion on the Fe-coral surface (H_2O or OH ligand → arsenate ligand).

Figure 4 indicates the effect of pH on the arsenic adsorption onto the Fe-coral. The arsenic adsorption was almost unaffected by an initial pH in the 2–10 range, and at a pH higher than 10 the adsorption was considerably decreased. In all of the runs in Fig. 4 (except the runs with initial pH > 10), the pH in the aqueous phase after equilibrium was 8.0–8.5. The calcium carbonate and the other minerals consisting of the coral can be slightly dissolved in the aqueous phase, and serve as a pH buffer, keeping the pH condition in the aqueous phase 8.0–8.5. Such a self-buffering effect of Fe-coral causes the independence of arsenic adsorption on the pH change of the solution. Consequently, the present arsenic adsorption method using Fe-coral proved to surpass the others such as the red mud method and the activated carbon method (*3*, *7*) with respect to a usable pH range.

Figure 5 shows the effect of coexisting anions in the aqueous phase on the arsenic adsorption. When chloride, nitrate, sulfate, perchlorate, or ace-

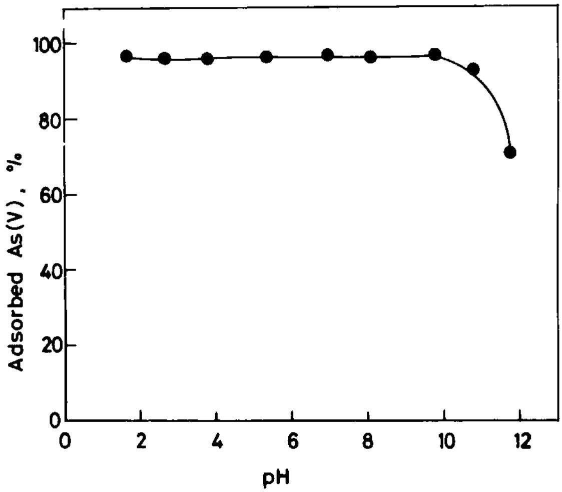

FIG. 4. Effect of pH. The aqueous phase initially contained 1.0 ppm arsenic(V), and the pH was adjusted by the use of 0.1 *M* hydrochloric acid and 0.1 *M* aqueous sodium hydroxide solution. Four-time treatment of Fe-coral was used.

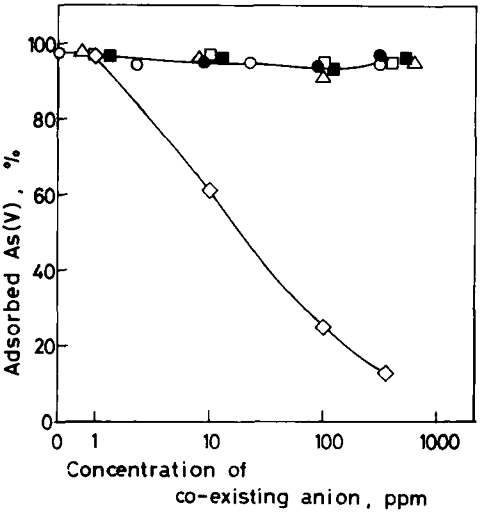

FIG. 5. Effect of coexisting anion. The aqueous phase initially contained 1.0 ppm arsenic(V) as well as NaCl (○), $NaNO_3$ (△), Na_2SO_4 (●), $NaClO_4$ (□), CH_3COONa (■), or NaH_2PO_4 (◇). Four-time treatment of Fe-coral was used.

tate was added (1-500 ppm) in the aqueous phase, the arsenic adsorption was sufficiently free of the influence of these coexisting anions. It is reported that in the red mud and activated carbon methods, the perchlorate, nitrate, and sulfate considerably depressed arsenic adsorption (*3*, *7*). Therefore, the present arsenic adsorption method using Fe-coral proved to be much superior to conventional methods with respect to interference by coexisting anions.

However, in the addition of phosphate anion in the aqueous phase (HPO_4^{2-} is the main species under a pH around 8), the adsorption of arsenate was greatly influenced. The arsenic adsorption was decreased with an increase in the phosphate concentration in the aqueous phase. Accordingly, it was found that although the addition of a hydrophobic anion such as perchlorate and nitrate as well as that of a hydrophilic anion such as chloride, acetate, and sulfate did not affect the adsorption nature, the phosphate caused an exceptional depression effect. This fact suggests strongly that arsenic adsorption proceeds not through a simple electrostatic interaction but through the ligand-exchange reaction as described before; therefore, only phosphate affects the arsenate adsorption due to the similarity of the ion structure.

TABLE 1
Desorption of Arsenic(V) under Various pH Conditions[a]

Shaking time (h)	Desorption (%)[b] at pH 3.5	5.0	7.5	8.5	9.9
16	1.9	2.8	2.4	3.1	3.1
43	1.8	3.0	2.4	2.8	2.5
91	2.0	2.2	2.1	2.3	1.9

[a] The pH of stripping solution was adjusted by use of 0.1 *M* hydrochloric acid and 0.1 *M* aqueous sodium hydroxide solution.

[b] Ratio of desorbed arsenic amount.

As shown in Table 1, the arsenic adsorbed on the Fe-coral was hardly desorbed in contact with an aqueous solution under various pH conditions (3.5–10). This result means that the arsenic adsorbed onto Fe-coral is hardly leached out when the Fe-coral is placed in a disposal dam.

Figure 6 shows the breakthrough curve in a column operation using Fe-coral. The adsorption capacity, μg of adsorbed arsenic per 1 g dry coral,

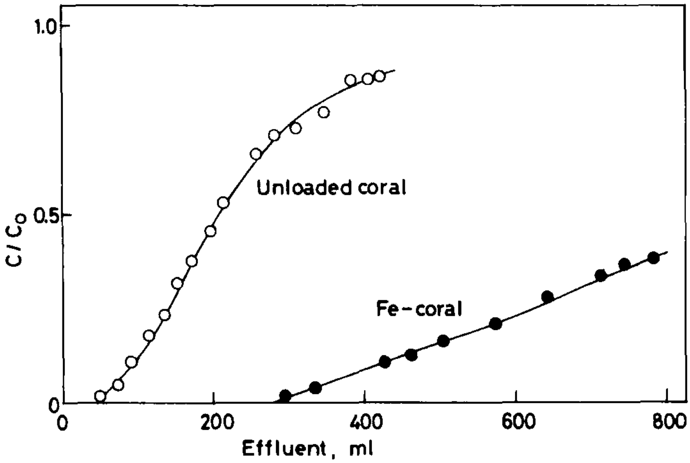

FIG. 6. Breakthrough curve of arsenic(V) on column operation. C_0 and C denote the initial concentration of arsenic (1.0 ppm) and the concentration in each effluent fraction, respectively. One-time treatment of Fe-coral was used.

was calculated from the curve to be ~15 μg/g, in good agreement with the results obtained from the batchwise experiment mentioned before. This result suggests that the present arsenic adsorption method can be successfully applied to column-type operation.

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