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# Iron(III) Hydroxide-Loaded Coral Limestone as an Adsorbent for Arsenic(III) and Arsenic(V)

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## Abstract

Trace levels of As(III) and As(V) in aqueous media were effectively adsorbed onto a coral limestone loaded by $Fe(OH)_3$. The adsorption of As(III) was almost comparable to that of As(V). The adsorption of As(III) and As(V) was almost independent of the pH of the aqueous phase (pH range: 3–10) because of a self-buffering effect of the coral. The addition of such anions as chloride, nitrate, sulfate, and acetate in the aqueous phase did not significantly affect the adsorption of As(III), whereas the addition of phosphate brought about a great decrease in the adsorption. The arsenic adsorption was effectively applied to the column method. Unloaded coral itself was effective as an adsorbent for As(V) when Fe(III) coexisted in the aqueous solutions.

## INTRODUCTION

In Japan, the arsenic level of water must be controlled to less than 0.5 mg/L in wastewater and to 0.05 mg/L in natural water. In order to reduce the arsenic content in industrial wastes to meet the standards, wastewater treatment processes are necessary to remove arsenic from the wastes.

In a previous paper (*1*) we reported the adsorption of As(V) by using a coral limestone loaded by $Fe(OH)_3$ (abbreviated Fe-coral), and we considered the following three points: 1) solid–liquid separation, 2) independence of adsorptivity on pH, and 3) cost. Our method has advantages compared to such conventional methods as coprecipitation with $Fe(OH)_3$ flocs (*2*, *3*) as well as adsorption on activated carbon (*4–6*), activated alumina (*7*), red mud (*8*), $MnO_2$ (*9*), and Fe(III)-loaded chelating resin (*10*).

In the present work we studied the adsorption of arsenic by using Fe-coral with particular emphasis on As(III) adsorption, and applied the adsorption behavior to the column method. The Fe-coral was found to be an excellent adsorbent for As(III); its adsorptivity was comparable to that of As(V).

It is known that the adsorption of As(III) is relatively difficult compared to As(V) adsorption. When activated carbon is used as an adsorbent, As(III) itself is scarcely adsorbed, but if it is oxidized to As(V), then adsorption takes place (*5*). In the coprecipitation method (*3*) and adsorption by activated alumina (*7*), the adsorption of As(III) is greatly dependent on pH, so that the optimum pH range is very limited. By the use of Fe-coral, As(III) was well adsorbed under a wide range of pH values, similar to the adsorption of As(V).

## EXPERIMENTAL

### Preparation of Fe-Coral

The coral limestone used was Porelime (Tokunoshima Coral Reef Co., Ltd., Japan), and its particle size was adjusted to 5–8 mesh and 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 200 mL of an aqueous solution containing 2 wt% $FeCl_3$ for 1 day. Then the particles loaded by $Fe(OH)_3$ were separated, rinsed with water, dried (100°C), and sieved on 120 mesh to remove free hydroxide particles generated as a by-product, resulting in the preparation of Fe-coral. The amount of iron loaded on the coral was ca. 1.0 mg/g.

### Adsorption of Arsenic

0.416 g sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) was dissolved in 100 mL water for the preparation of 1000 mg/L As(V) standard solution. 0.173 g sodium arsenite ($NaAsO_2$) in 100 mL water was the As(III) standard (1000 mg/L).

1.0 g Fe-coral was shaken with an aqueous solution (20 mL) containing As(V) or As(III) at 25°C for a definite period. After removing the Fe-coral, the concentration of arsenic remaining in the aqueous solution was determined by atomic absorption spectrophotometry using a Nippon Jarrel Ash AA-855 with a flameless atomizer unit FLA-1000.

### Column Operation

A glass tube of 29 mm i.d. was packed with 20 g Fe-coral to give a column of 17 mL in volume and 25 mm high. An aqueous solution containing several concentrations of As(V) or As(III) was passed through the column at room temperature (23–26°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

### Adsorption of As(V) and As(III)

Figures 1 and 2 show time courses of the adsorption of As(V) and As(III), respectively. Fine particles (8–120 mesh) of Fe-coral exhibited a higher adsorption ability than did coarse particles (5–8 mesh). The fine particles were used later. The adsorption reached equilibrium after 8-h shaking for As(V) and after 24-h shaking for As(III). It is known that As(III) coprecipitates with $Fe(OH)_3$ without oxidizing to As(V) (*3*). It is presumed that in the present system of Fe-coral the oxidation of As(III) does not take place.

### Adsorption Isotherm

Figure 3 shows the adsorption isotherms of As(V) and As(III) by the use of Fe-coral. These adsorption isotherms are almost linear. Thus, the adsorption mode is of a typical Freundlich isothermal nature. As(V) was somewhat more adsorbed than As(III). When unloaded coral was used as the adsorbent, the adsorption of As(III) was greatly decreased.

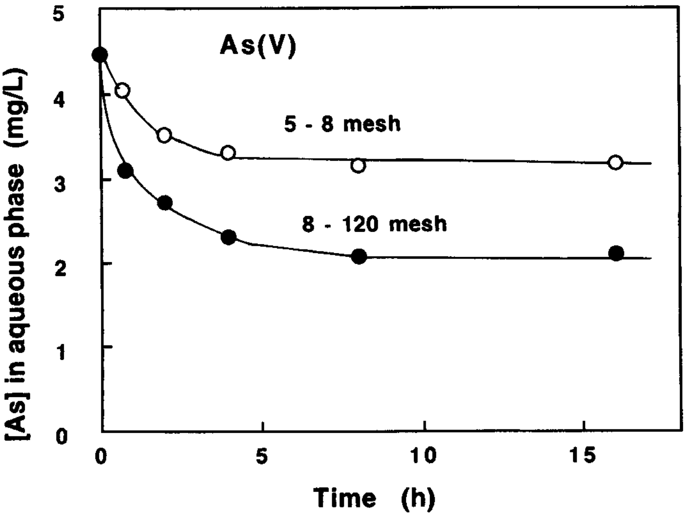

FIG. 1. Adsorption of As(V) by Fe-coral.

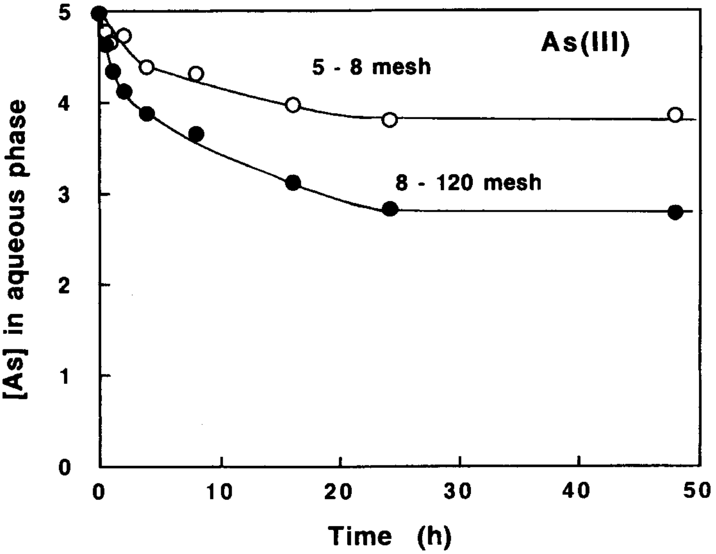

FIG. 2. Adsorption of As(III) by Fe-coral.

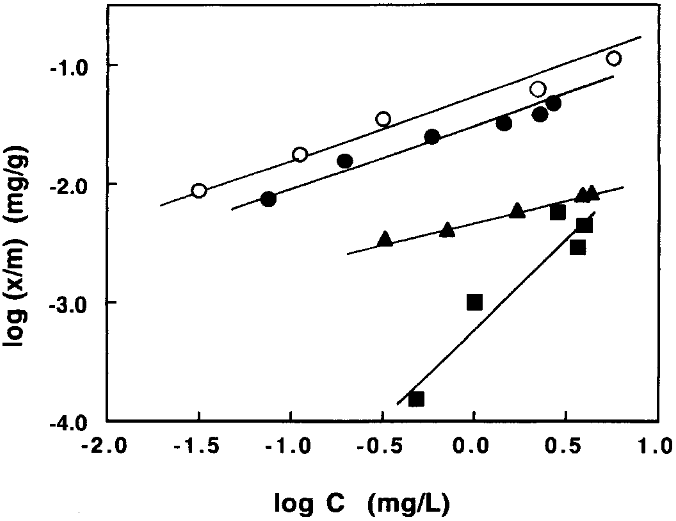

FIG. 3. Adsorption isotherms for various adsorbents [Fe-coral: ○ (As(V)), ● (As(III)); unloaded coral: ▲ (As(III)); Kansuiseki: ■ (As(III))]. *C* and *x*/*m* denote the equilibrium concentration of arsenic in solution and that in adsorbent, respectively.

The mechanism of the preparation of Fe-coral is presumed to be as follows (*1*). The following reaction takes place on the surface of coral when it is soaked in an aqueous $FeCl_3$ solution:

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

The colloidal $Fe(OH)_3$ generated is effectively deposited onto the porous surface of the coral, leading to the preparation of Fe-coral.

When Kansuiseki (Nittofunka Kogyo Co., Ltd., Japan; calcite, $CaCO_3 > 99\%$) was used as a reference support of $Fe(OH)_3$, the adsorption was considerably decreased. Consequently, the coral is greatly advantageous as an effective support for $Fe(OH)_3$ because of its porosity and chemical activity.

## Effect of pH

Figure 4 indicates the effect of pH on the adsorption of arsenic onto Fe-coral. The adsorption of As(III) was almost independent of the initial pH in the 3–10 range, similar to As(V) adsorption. This is the remarkable feature of Fe-coral which cannot be attained by using other separation methods such as coprecipitation with $Fe(OH)_3$ (*2*, *3*) and adsorption by activated carbon (*4*–*6*) and activated alumina (*7*).

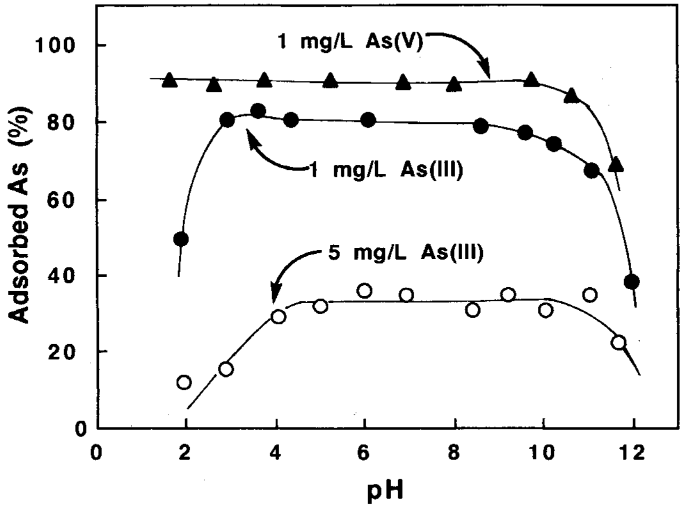

FIG. 4. Effect of pH. The aqueous phase initially contained a definite amount of arsenic (indicated in the figure), and the pH was adjusted by using 0.1 *M* hydrochloric acid and 0.1 *M* aqueous sodium hydroxide.

The p*K* values for $H_3AsO_3$ (As(III)) at 25°C are 9.22, 12.1, and 13.4. Therefore, under neutral and acidic conditions, As(III) exists as a neutral species and cannot be adsorbed on the adsorbent based on ionic interaction. Moreover, under alkaline conditions such adsorbents as activated carbon and activated alumina lose their ability because of the decrease in the surface positive charge. As a result, the range of optimum pH for adsorption becomes very limited in the above cases.

In all of the runs in Fig. 4 (except the runs with an initial pH > 10), the pH in the aqueous phase after equilibrium was 8.0–8.5. Calcium carbonate (i.e., coral) can be dissolved in the aqueous phase to some extent and serves as a pH buffer, especially near the coral surface. Accordingly, adsorption of As(III) is not affected by the initial pH due to this self-buffering effect.

## Effect of Coexisting Anion

Figure 5 shows the effect of coexisting anions in the aqueous phase on As(III) adsorption. As with As(V) adsorption (*1*), only phosphate interfered with the adsorption of As(III), while chloride, sulfate, nitrate, and acetate hardly affected the adsorption.

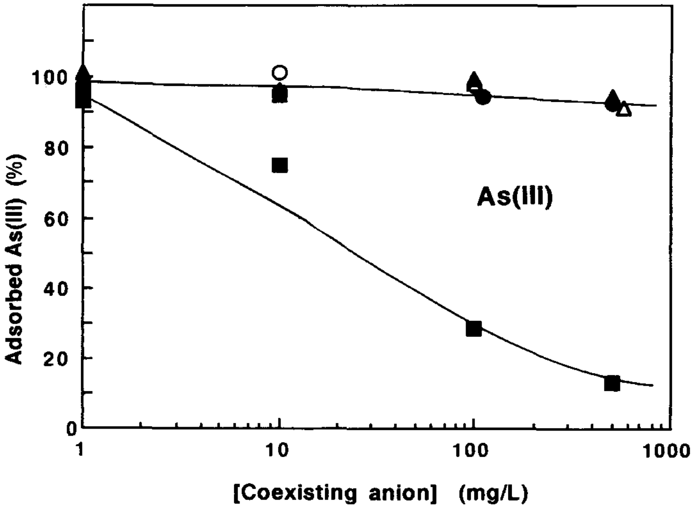

FIG. 5. Effect of coexisting anion. The aqueous phase initially contained 1.0 mg/L of As(III) as well as NaCl (●), $NaNO_3$ (△), $Na_2SO_4$ (○), sodium acetate (▲), or $Na_2HPO_4$ (■).

## Column Method

Figure 6 shows the breakthrough curve of As(V) using Fe-coral on passing sample solutions of various concentrations of As(V). The adsorption capacity, μg of adsorbed arsenic per 1 g dry coral, was calculated from the curve to be ca. 15 μg/g; this is in good agreement with the value obtained from the batchwise experiment mentioned before.

Figure 7 shows the breakthrough curve of As(III). The adsorption capacity was 13 μg/g, in good agreement with the value of the batchwise experiment.

Adsorption by Fe-coral can be successfully applied to the column method. When the Fe-coral adsorbed by arsenic was shaken with an arsenic-free aqueous solution under various pH conditions (3.5–10) for a long time (>100 h), the arsenic (either As(V) or As(III)) was scarcely desorbed. We believe that landfill disposal of Fe-coral after arsenic-adsorption treatment is the best method of disposal when the difficulty in desorption, its cheapness, and the simplicity for solid–liquid separation are taken into account.

Arsenic-polluted natural water occasionally contains a high concentration of Fe(III). At Suzuyama, an old mine in Kagoshima, 0.8 m$^3$/min pol-

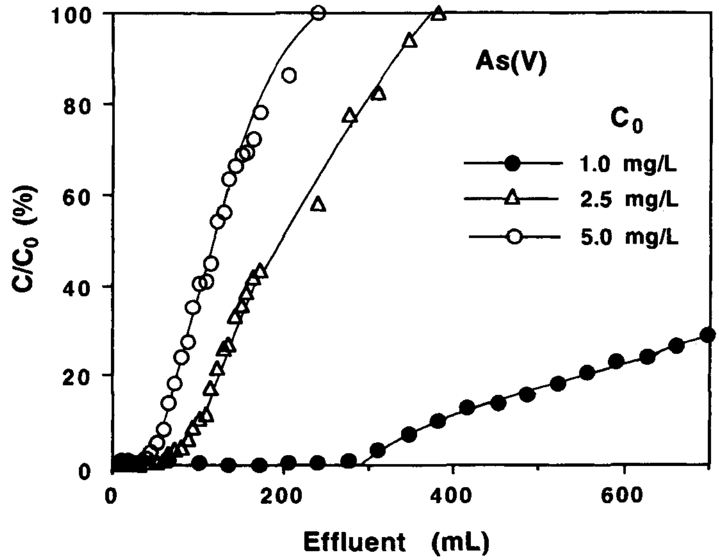

FIG. 6. Breakthrough curve of As(V) on a column operation using Fe-coral. $C_0$ and $C$ denote the initial concentration of As(V) and the concentration in each effluent fraction, respectively.

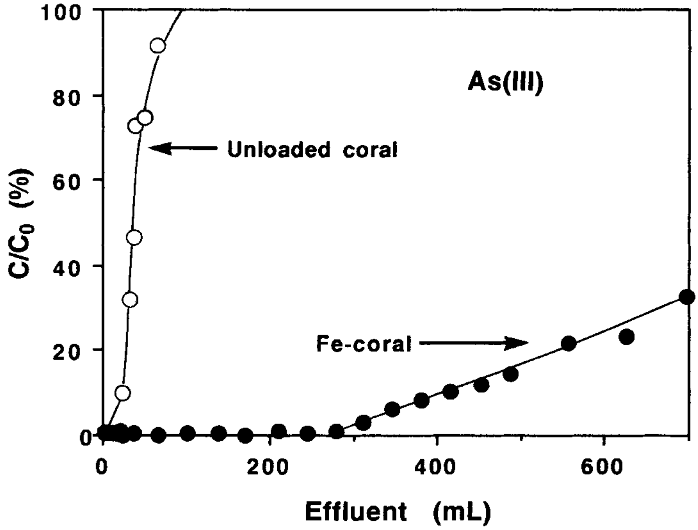

FIG. 7. Breakthrough curve of As(III) on a column operation using Fe-coral. $C_0$ was 1.0 mg/L.

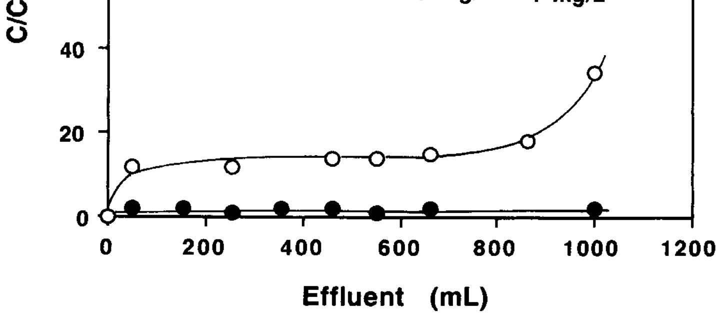

FIG. 8. Breakthrough curve of As(V) by the use of a sample solution containing Fe(III) and As(V). 20 g of unloaded coral was used.

luted water flows out, and it contains 5–20 mg/L Fe(III) and 0.2 mg/L arsenic. An aqueous solution containing both Fe(III) and As(V) was passed through a column of the unloaded coral. Figure 8 shows the breakthrough curve of As(V); the column was clogged with colloidal $Fe(OH)_3$ generated after ca. 1000 mL effluent had been passed. When an aqueous solution contained 5 mg/L Fe(III) was used, a considerable breakthrough of As(V) was observed. However, in the case of a 10 mg/L Fe(III) solution, As(V) was completely adsorbed on the column. In both cases, iron was not observed in the effluents. If a more sophisticated device can be designed, the coral-limestone is applicable as an adsorbent for such polluted water.

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