Article

Adsorptive Removal of Arsenic by Zirconium Ion-Loaded Orange Waste Gel

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Abstract

Adsorption gel (SOJR gel) was prepared from orange juice residue by means of saponification with calcium. Because the zirconium is known to have a high affinity to As(V), zirconium-loaded SOJR was investigated for its adsorption behavior for As(V) in water. It exhibited a high adsorption at pH around 2 to 5. The maximum loading capacity for As (V) onto the gel was 1.11 mol/kg.

Key words: adsorption, Arsenic, zirconium, orange juice residue

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1 Introduction

Arsenic is a toxic unwanted chemical constituent posing epidemiological problems to human health. Arsenic pollution has been seriously observed not only in various mineral and chemicals processes but also in some ground water or hot spring water over the large area in Asian countries such as Bangladesh, West Bengal in India, Inner Mongolia in China, and Japan as well. Therefore, the effective removal of arsenic is strongly demanded at a low cost.

The state of arsenic is pentavalent and trivalent. In the solution, the pentavalent and trivalent arsenic exist as anionic species of arsenate ion and arsenite ion, respectively. In environment, the other anions such as sulfate, chloride, and carbonate are contained together with arsenic ions, making it difficult to selectively remove small amount of arsenic using anion-exchange resin. To date, various methods like ion exchange, adsorption, precipitation and complexation are used for removing arsenic.[1-3] The precipitation method includes precipitation with lime, co-precipitation with ferric sulfate, alumina precipitation, and precipitation as sulfide using either sodium sulfide or hydrogen sulfide. Although, among these methods, iron co-precipitation method has been reported to be the most successful in lowering arsenic content to the drinking water standard level, it still suffers from a post treatment problem due to the alkaline sludge generation.

In this study, As(V) ion was removed by the zirconium-ion-loaded orange juice residue gel, in which zirconium ion was immobilized on pectic acid contained in the waste orange juice residue since zirconium has a high affinity to As(V) [4, 5]. The adsorption behavior for As(V) under varying conditions was discussed.

2 Experimental

2.1 Preparation of the adsorption gel from saponified orange juice residue (SOJR)

Two hundred grams of crude orange waste was mixed together with 800 cm^3 of saturated calcium hydroxide solutions and crushed into fine particles using juice mixer. Here calcium hydroxide not only facilitates the saponification but also enables to bleach out chlorophyll and other low molecular weight compounds that hinder the adsorption. The suspension of saponified gel was repeatedly washed with distilled water followed by decantation until neutral pH and finally filtered. The wet cake of the saponified gel, which is abbreviated as SOJR here after, was dried in a convection oven at 60℃ for 72 h.

Since As(V) can not be directly adsorbed onto the gel, the SOJR gel was loaded with Zr(IV) prior to the adsorption of As(V). Two grams of the dried gel was shaken together with 1 L of 10 mM zirconium oxychloride solution at pH = 2.0 for 24 h at 30°C. The amount of zirconium loaded onto the gel was evaluated to be 1.95 mol/kg dry gel.

2.2 Batchwise adsorption test

In the batch wise adsorption tests, 25 mg of dried adsorbent was taken into a 50 mL conical flask together with 15 mL of corresponding aqueous solution. The pH of the aqueous solutions was adjusted by HCl or NaOH together with 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulfonic acid (HEPES) as buffer reagent. The flask was shaken vigorously in a thermostated shaker at 30°C at 150 rpm for 24 h to ensure the equilibrium to be attained. The initial and equilibrium concentrations of metal ions were measured by using Shimadzu Model ICPS-8100 ICP/AES spectrometer.

The percentage adsorption (A %), defined as the ratio of decrease in metal concentration in apueous solution before and after adsorption (C_i - C_e) to its initial concentration (C_i), was calculated according to Eq. (1)

$$A\% = (C_i - C_e)/C_i \times 100 \tag{1}$$

The amount of adsorption (q/mol kg^{-1}) was calculated according to Eq. (2) from the metal concentrations before and after the adsorption.

$$q = [(C_i - C_e)/W]\,(L) \tag{2}$$

In the above equations, q represents the amount of metal uptaken per unit mass of the adsorbent (mol/kg), L the volume of the test solution (dm^3), W the dry mass of the adsorbent (g), C_i and C_e the initial and the final concentrations (mmol/dm^3), respectively.

2.3.Column test

For the adsorption test using column, glass beads, cotton, and Zr-SOJR (50 mg) were packed in a glass column (diameter = 8 mm) through which As(V) solution (0.2mM) at pH 3.3 was passed at a constant flow rate of 3 mL/h after conditioning the column overnight. The effluent was collected using a fraction collector (Bio-Rad Model 2110) at time intervals of 1 h. After washing the column with ion-exchanged water, the adsorbed As(V) was eluted with 1 M NaOH at the same flow rate.

3 Results and Discussion

3.1 Effect of pH on As(V) adsorption

Figure 1 shows the relationship between % adsorption of As (V) as well as % elution of the loaded zirconium and equilibrium pH in the adsorption of As(V) on Zr-SOJR gel at an initial concentration of 0.20 mM. It is seen from this figure that the pH of the aqueous solution plays as the important variable for adsorption. The optimum pH for the adsorption of As(V) was observed at pH=2-5. At pH less than 1, small amount of the loaded zirconium was found to be leaked, whereas at around the optimum pH, Zr(IV) was confirmed to be strongly loaded onto the adsorbent.

3.2 Adsorption isotherm of As(V) ion

Figure 2 shows the adsorption isotherm of As (V). The amount of arsenic adsorbed increases with increasing concentration of arsenic and tends to approach a constant value at the concentration greater than 5 mM. From this constant value, the maximum adsorption capacity of As(V) was evaluated as 1.11 mol/kg. From the stoichiometry of the loaded Zr (IV) and As(V), it can be concluded that Zr(IV) forms a complex with As(V) of the mole ratio of 2:1.

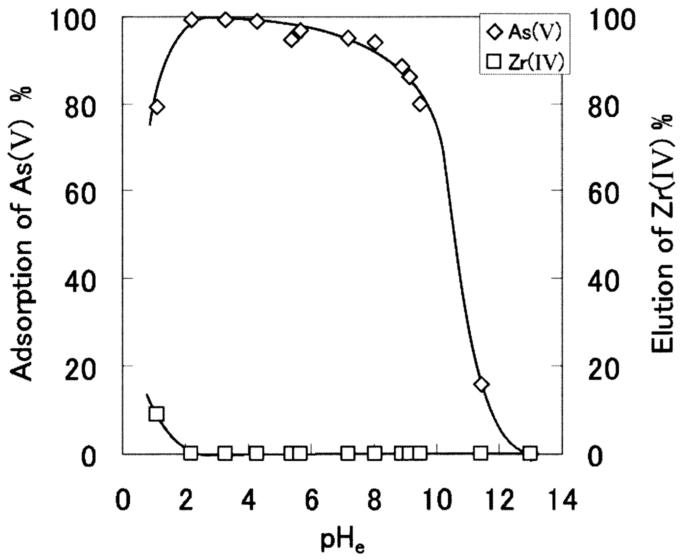

Fig.1 Adsorption of As(V) on the Zr-SOJR as a function of equilibrium pH. Weight of the gel = 25 mg. Volume of the aqueous solution = 15 cm^3. Initial As(V) concentration = 0.20 mM

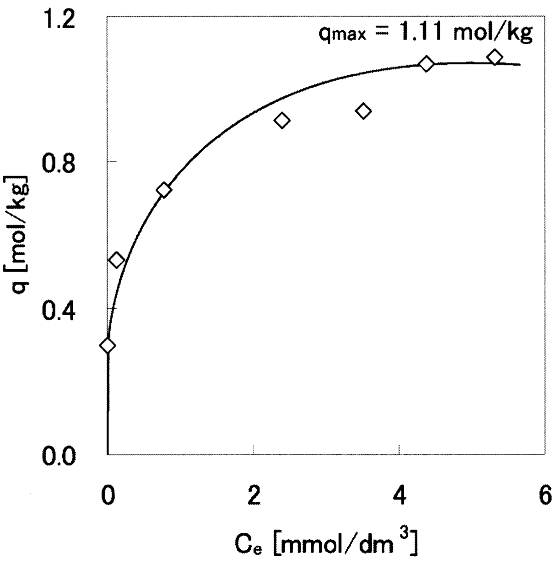

Fig.2 Adsorption isotherm of As(V) on Zr-SOJR. Volume of the aqueous solution = 15 cm^3. Weight of the gel = 25 mg. pH = 3.3

3.3 The competitive adsorption with other metal ions.

Figure 3 shows the effect of pH on the adsorption of As(V) in the presence of other anionic species. From this figure, it is clear that the adsorption of As(V) is not affected by the presence of any other anionic species, the concentrations of which are as much as 10 times to that of As (V), revealing that adsorption of As(V) ion is highly selective and independent of other anions.

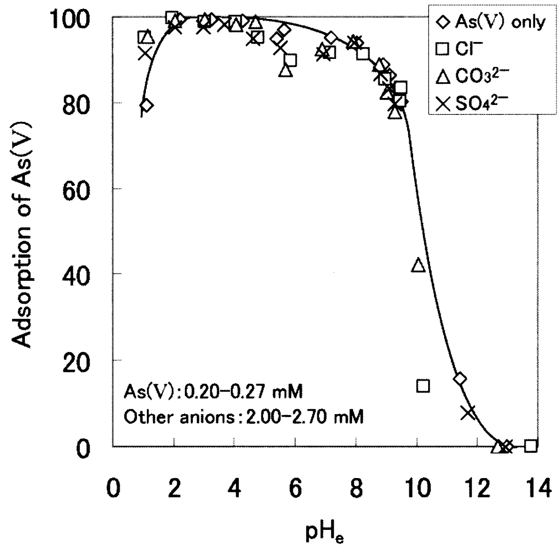

Fig.3 Effect of pH on the adsorption of As(V) in the presence of excess amount of chloride, carbonate or sulfate ion.

3.4 Breakthrough followed by elution tests using a packed column.

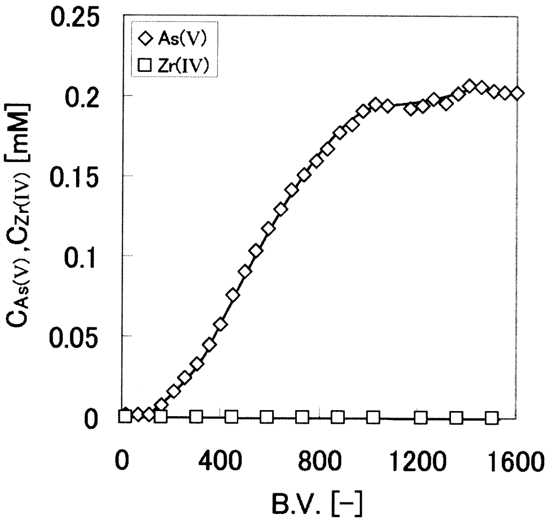

Fig.4 Breakthrough profile of As(V) using the column packed with Zr-SOJR gel.(C_0 = 0.20 mM)

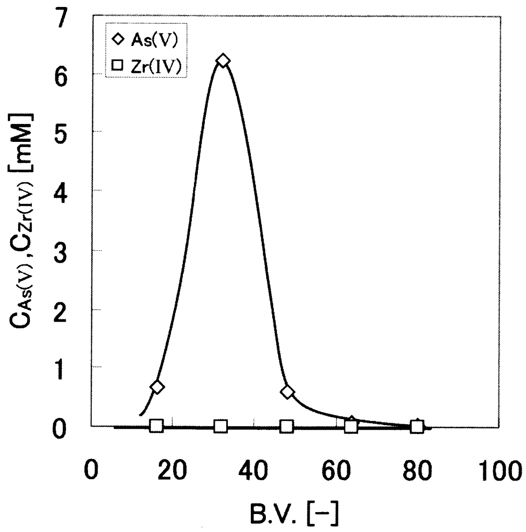

Fig.5 Elution profile of As(V) from the packed column with 1M-NaOH

Figures 4. and Fig. 5 show the breakthrough and elution profiles of As(V), respectively. The breakthrough of As(V) occurred at a bed volume(BV) of 200, and equilibrium was attained at around 1,400 BV, during which no leakage of Zr(IV) was observed. From this figure, the equilibrium binding capacity of As(V) was evaluated as 0.47 mol/kg. On the other hand, from Fig. 5, it was found that As(V) was eluted with a recovery percentage of 95% within 60 BV while the immobilized Zr(IV) was not leaked from the column, indicating that Zr-SOJR was possible to be reutilized as As(V) adsorbent.

From the above-mentioned experimental results, it is clear that use of zirconium loaded SOJR can be very promising for the adsorptive removal of As(V) from aqueous system. Contrary to the other Zr-loaded adsorbents, the starting material for adsorbent employed in this study is orange juice residue, a biomass, which is widely available and incurs almost no cost. In addition, the preparation of the gel is easy and economic. Furthermore, since the loaded Zr(IV) was adsorbed strongly onto the gel, no leakage of Zr(IV) was observed during the elution of As (V) which enables us to reuse the gel for many times.

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