

Synthesis of arsenic adsorbent using graft polymerization

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Abstract

Fibrous arsenic (As) adsorbent was synthesized by loading zirconium (Zr) on fibrous phosphoric adsorbent that was directly synthesized by radiation-induced graft polymerization of 2-hydroxyethyl methacrylate phosphoric acid on polyethylene-coated polypropylene nonwoven fabric. Zirconium reacted with phosphoric acid grafted in the polyethylene layer. Zirconium density of the resulting adsorbent was 4.1 mmol/g. The breakthrough curve of As(V) adsorption was independent of the flow rate up to 1300 h⁻¹ in space velocity. The total capacity of As(V) was 2.0 mmol/g-adsorbent at pH of 2. The adsorbed Zr(IV) could be evaluated by 0.4 M sodium hydroxide solution because negligible Zr(IV) could be found in the eluted solution.

Key word: Loading zirconium, Radiation-induced graft polymerization, Arsenic(V) adsorption

1. Introduction

Removal of toxic metal from the industrial wastewater and mine water is important task to preserve environment. Arsenic (As) is a naturally occurring substance in the earth, and it very widely distributes in the environment more often as arsenic sulfide or as metallic arsenates and arsenides. The contamination of streaming water and ground water with arsenic oxide are widely found. The common purification method is precipitation by adding coagulant agent into the contaminated water. However, the produced precipitation should be carefully treated due to the toxicity of As. According to the basic environment law, which provides for the water quality guidelines for public waters, As should not be discharged at concentration higher than 0.1 ppm and its content in the environment should not exceed 0.01 ppm. Thus, the removal of As is absolutely necessary. On the point of view of adsorbent synthesis, radiation induced graft polymerization (RIGP) is a powerful technique to introduce the chelate function into variety shapes of conventional polymers such as fibers, particle and membrane. Especially,

fibrous adsorbent prepared by RIGP realized 100 times higher space velocity (SV) than that commercialized particle-adsorbent[1].

A ligand exchange adsorbent is effective for the removal of arsenic oxide. In the past, the ligand exchange resin was synthesized by copolymerization of divinylbenzene and glycidyl methacrylate having phosphoric acid[2]. The maximum space velocity for the removal of As is 10 h^{-1} in the resin-packed column. In the RIGP, irradiation of γ -ray or electron beam is capable of creating radicals in polymer. This initiation of the radiation processing can be done at room temperature and less than without any chemical reagents.

The objective of this study is dealing with the development of new zirconium(Zr) loaded fibrous phosphoric adsorbent (ZrPA-ad) by using RIGP. In removal of trace amounts of As(V) in a huge volume of water, a breakthrough capacity is much more important than an equilibrium capacity because the latter is usually measured by the batch method at high concentration levels of As(V). Taking into account the fact that large equilibrium capacities do not always mean large breakthrough capacities, we examined the detailed behavior of ZrPA-ad in adsorption and elution of As(V) by column method.

2. Experimental

2.1 Synthesis of Arsenic adsorbent

Fibrous Zr-loaded phosphoric acid adsorbent (ZrPA-ad) was synthesized by grafting of monomer having phosphoric acid onto nonwoven fabric and Zr(IV) was loaded on it (Figure 1)[3]. The nonwoven was composed of polyethylene-coated polypropylene. The graft polymerization was carried out by contacting the nonwoven fabric irradiated by 200kGy electron beam with 30% monomer solution of pure water and methanol for 8 hours at 60°C . The resulting phosphoric acid adsorbent (PA-ad) had 427% grafting degree that corresponded to 5.2 mmol-phosphoric acid per one gram of adsorbent. Then,

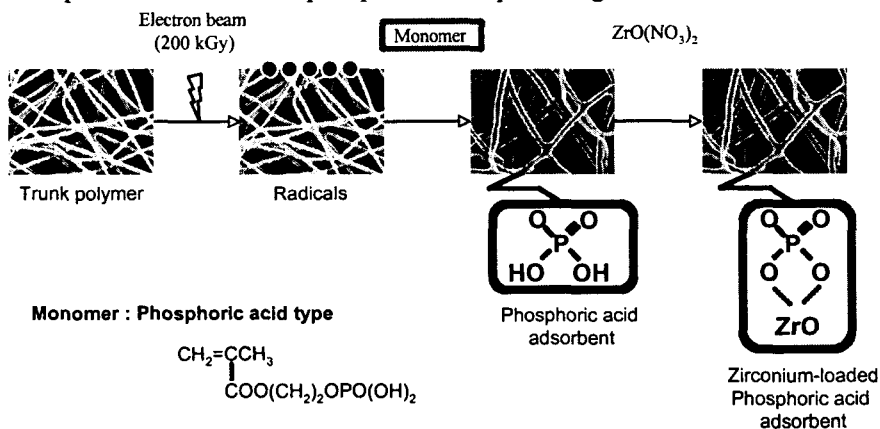


Fig. 1 Preparation scheme of Arsenic adsorbent

Zr(IV) was loaded onto PA-ad by the contacting of Zr(IV) solution with PA-ad-packed column, 7mm in inner diameter. The volume of the 0.05 g adsorbent in the column was 0.4 cm^3 , which was regarded as 0.4 ml bed volume (BV). The Zr(IV) solution was prepared by dissolving zirconium nitrate oxide dihydrate, $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in the nitric acid solution after pH was adjusted to 1. The Zr(IV) solution of 10 mM was pumped into the column with the flow rate of 100 ml/h until the outlet concentration of Zr(IV) was equal to 10 mM. Finally, the ZrPA-ad in the column was washed with distilled water until acid free.

2.2 Column mode adsorption and elution of arsenic

The solution of As(V) was prepared by dissolving analytical grade of sodium arsenate dibasic heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$). The pH was adjusted by adding nitric acid and sodium hydroxide. The arsenic solution was put in ZrPA-ad column by changing feeding rate up to 1300 h^{-1} in SV. The adsorbed As on the ZrPA-ad was eluted by pumping 0.4 M sodium hydroxide into the column. The breakthrough point was defined as feeding volumes (BV) at the concentration ratio of pumping solution to effluent C/C_0 up to 0.05, where C_0 and C represent concentrations of arsenic in the feeding solution and in the column effluent, respectively.

3. Result and discussion

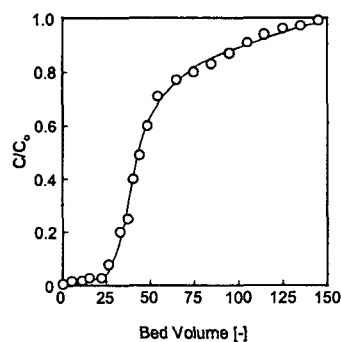
3.1 Preparation of ZrPA-adsorbent

The Zr(IV) was first loaded on the PA-ad by pumping Zr(IV) solution into the PA-ad-packed column with 250 h^{-1} in SV. Figure 2 shows the adsorption characteristic of Zr(IV) on PA-ad. Almost all of Zr(IV) was adsorbed on the PA-ad in the initial 25 BV. Totally, 0.21mmol of Zr(IV) was adsorbed on 0.05 g of PA-Ad after 150 BV feeding. The loading rate of Zr(IV) was 40 times faster than resin adsorbent which was reported by Zhu et al[2].

As a result, the density of the loaded Zr(IV) on PA-ad was 4.1mmol/g. This density was roughly 6 times higher than that of the cross-linked resin having phosphoric acid.

3.2 Effect of pH on arsenic adsorption

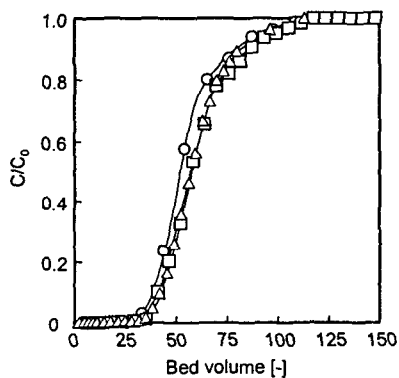
The breakthrough of ZrPA-ad was evaluated at pH range from 1 to 9 by pumping 5 mM arsenic solution into the ZrPA-ad column. The breakthrough



point was 32 BV at the pH 1 and 3, and went up to 38 BV at pH 2. Further increment of pH gradually reduced breakthrough point. At pH 7 and 9 the breakthrough points were 20 BV. The maximum breakthrough capacity was calculated to 1.5 mmol/g at pH 2. The total capacity at this pH range was 2.0 mmol/g. The two moles of Zr(IV) corresponded to adsorption of one mole of As(V). Although the breakthrough point and capacity were decreased in alkali area, the performance of ZrPA-ad could be maintained in acid area, breakthrough points and capacity respectively.

3.3 Effect of flow rate on arsenic adsorption

The breakthrough curves were observed with three different flow rates of 75, 250 and 1300 h⁻¹ in SV by pumping 5 mM As(V) solution into the ZrPA-ad column at pH 2. The breakthrough curves are essentially independent of the flow rates at 75 and 250 h⁻¹ as shown in Figure 3. The breakthrough point slightly decreased at the extremely high flow rate of 1300 h⁻¹. This result indicates that the fastest flow rate of 1300 h⁻¹ is the upper limit of As(V) adsorption with ZrPA-ad column. However, the flow rate of 1300 h⁻¹ is 130 times faster than that of general granular resin packed column. Fe (III)-loaded iminodiacetic acid resin exhibited poor kinetic adsorption of As(V) even at a flow rate of 2 h⁻¹ in SV, and its breakthrough capacity was about 0.085 mmol/g. In this work, the breakthrough capacity of three flow rates gave 40, 38, and 35 BV. These capacities corresponded to 1.4, 1.3 and, 1.2 mmol/g of As on ZrPA-ad. The total capacities were 2.0, 2.0 and 2.1 mmol/g adsorbent for 75, 250 and 1300 h⁻¹, respectively.



3.4 Elution of adsorbed As(V)

As(V) adsorbed onto ZrPA-ad column could be eluted by 0.4 M solution of sodium hydroxide. Negligible Zr(IV) could be found in the solution. In the case of elution, flow rate was 25 times higher than that of Zr(IV)-loaded phosphoric acid chelating resin. The water contents of ZrPA-ad were 120 and 130 at pH of 1 and 11, respectively. It means the adsorbent volumes in adsorption and elution were maintained a certain volume. On the point of application view, damage of the column by swelling of adsorbent can be avoided by using this adsorbent.

4. Conclusions

The ZrPA-ad was prepared by Zr(IV) loading on the fibrous phosphoric adsorbent, which was synthesized by radiation-induced grafting on polyethylene-coated polypropylene nonwoven fabric. The phosphorus function was introduced only to the outer layer of polyethylene and Zr(IV) was loaded on the phosphoric acid. This adsorbent should have a rapid adsorption rate and high capacity for arsenic ion. The breakthrough curve of As(V) adsorption was independent of SV up to 1300 h^{-1} . The maximum capacity of ZrPA-ad for As(V) was $2.0 \text{ mmol/g-adsorbent}$. The adsorption rate of ZrPA-ad was 130 times faster and the capacity was 6 times higher than those of adsorbent resin. The adsorbed As(V) on ZrPA-ad was quantitatively eluted with 0.4 M sodium hydroxide. The escape of Zr(IV) from ZrPA-ad was negligible in the As(V) adsorption and elution processes. The ions of chloride and nitrate reduced 30% and 40% the breakthrough capacity of As(V) adsorption, respectively.

Reference

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