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Preparation of porous resin loaded with crystalline hydrous zirconium oxide and its application to the removal of arsenic

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Abstract

A porous resin loaded with monoclinic or cubic hydrous zirconium oxide was prepared by incorporation of $ZrOCl_2 \cdot 8H_2O$ into porous spherical polymer beads followed by hydrolysis and hydrothermal treatment of the zirconium salt. Hydrous zirconium oxide appeared to deposit inside the pores with relatively large diameter. The adsorption capacity and distribution coefficients for As(III) and As(V) were determined by batch procedures. The hydrous zirconium oxide-loaded resin (Zr resin) showed a strong adsorption for As(V) at slightly acidic to neutral pH region while As(III) was favorably adsorbed at pH around 9 to 10. The removal of low concentrations of arsenic from the model effluents to meet the demand of Japanese industrial effluent standard (0.1 ppm) was successfully achieved by the column operation packed with the Zr resin. The Zr resin was regenerated by treatment of the column with 1 M sodium hydroxide followed by conditioning with 0.2 M acetate buffer solution. The amount of zirconium leached out during the adsorption and regeneration cycles was negligibly small and the column can be used repeatedly.

Keywords: Hydrous zirconium oxide; Zirconium-loaded porous resin; Removal of arsenic

1. Introduction

Arsenic is one of the extremely toxic metal ions, which could increase the risk of lung, kidney and skin cancers [1]. Therefore the removal of trace arsenic from industrial effluents or drinking water systems has become of increasing importance. The standard allowances of concentration in an industrial effluent and drinking water in Japan have been adopted to be 0.1 ppm and 0.01 ppm, respectively in 1994. Co-precipitation with aluminum salt, lime and ferric oxide is most commonly employed for the removal of arsenic [2–4]. However, because of the solubility restrictions of precipitates, a small amount of arsenic ions tend to remain in the solution. In addition, coprecipitation process produces a wet bulky sludge and often requires troublesome filtration. On the contrary, column adsorption procedure is a promising method for the treatment of trace amount of toxic ions present in a large quantity of water due to the high concentration efficiency and ease in phase separation. Chelating polymer resins with sulfur containing ligands [5] and ferric ion chelated polymers [6–8] have been examined so far for

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the removal of As(III) and As(V). The former system is based on the high affinity of sulfur donor atom to As(III) and/or As(V) while the latter system involves a ligand exchange process between coordinated water and arsenic species.

Inorganic ion exchangers are one of the probable candidates due to their specific selectivity toward the certain anions [9–11]. Hydrous zirconium oxide has been known to have a remarkable selectivity to phosphoric ion [12]. In addition, it has high resistance against attacks by acids, alkalis, oxidants and reductants. Since phosphorus and arsenic commonly belong to group 5B elements, their ionic species and chemical properties are quite similar to each other. In fact acid dissociation constants of phosphoric acid and those of arsenic acid are mutually very close [13]. However, a detailed description of the adsorption of arsenic on hydrous zirconium oxide has not been reported so far. In addition, a common drawback of inorganic ion exchangers is the difficulty to obtain spherical beads of suitable size for the required applications. In order to overcome this difficulty, we have incorporated hydrous zirconium oxide into the pores of a porous polymer resin.

We have prepared hydrous zirconium oxide-loaded resin (Zr resin) by impregnation of zirconium alkoxide into porous polymer beads followed by hydrolysis of the alkoxide [14]. The obtained resin revealed a remarkable selectivity toward the adsorption of fluoride. In the present work zirconyloxychloride ($ZrOCl_2 \cdot 8H_2O$) was used as the starting material in place of zirconium alkoxide for economic reasons. The Zr-loaded resin showed a strong retainment of As(III) and As(V). The preliminary results have been communicated previously [15]. In this paper we deal with the detailed description of the work, i.e., the preparation and physicochemical properties of the Zr resin and its performances including adsorption capacity, distribution coefficient, and column treatment for As(III) and As(V).

2. Experimental

2.1. Measurements

The metal ion concentration was determined by an inductively coupled plasma atomic emission spectrometer (ICP–AES), SEIKO Model SPS-1200A. The following operating conditions were employed: RF Power 1.39kW; Integration time 1–2 s; Observing height 9.8 mm; Wavelength As = 228.812 nm, Zr = 339.198 nm. A digital pH meter, TOA HM-265 was used for the pH measurement. The pH values of solutions were adjusted with acetate buffer in the pH range of 3–6 and with ammonia/ammonium chloride buffer above pH 6. The x-ray diffraction of the crystalline zirconium samples was measured with Rigaku Roterflex Ru-300 RAD-C system. Pore distribution and specific surface area were measured with the gas adsorption type porosimeter, Micromeritics Asap-2400.

2.2. Chemicals and solutions

The polymer resin, Amberlite XAD-7 (Rohm and Haas Co.) was washed with dioxane in a Soxlhet extractor and then dried at 50°C under reduced pressure. Stock solutions of As(III) and As(V) were prepared by dissolving reagent grade $NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$ in deionized water.

2.3. Preparation of the hydrous zirconium oxide loaded resin

A solution containing 43.8 g zirconyloxychloride ($ZrOCl_2 \cdot 8H_2O$) in 250 ml of methanol was prepared. To this solution, 35.0 g of dried Amberlite XAD-7 beads were added and the mixture was placed in a dessicator under reduced pressure. After 30 min, methanol was evaporated off. To the dried residue, 150 ml of 28% ammonia solution was added and the contents were stirred for 5 h. Then 500 ml of water was added and the white precipitates so