Removal of As(III) and As(V) by a Porous Spherical Resin Loaded with Monoclinic Hydrous Zirconium Oxide

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A porous spherical resin loaded with monoclinic hydrous zirconium oxide was prepared and the physico-chemical properties were examined. The zirconium loaded resin showed a strong retainment of As(III) and As(V). The removal of low concentration of arsenic to meet the demand of industrial effluent standard (0.1ppm, ppm = mg dm^{-3}) was achieved by the column process with the present resin.

Since arsenic is one of the extremely toxic metal ions, the removal of trace arsenic from industrial effluents or drinking water systems has become of increasing importance. Co-precipitation with aluminum or ferric salt is most commonly applied to the removal of arsenic.[1-3] However, because of the solubility restrictions of the 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 filtration for final treatment. On the contrary, column adsorption procedure is a promising method for the treatment of trace ions in a large volume of water due to the high concentration efficiency and ease in phase separation. Chelating polymer resins with sulfur containing ligands[4] and ferric ion chelated polymers[5-7] have been examined for this purpose.

Inorganic ion exchangers are another candidates due to their specific selectivity toward the certain anions.[8-10] Hydrous zirconium oxide is known to have a remarkable selectivity to phosphate ion.[11] Since phosphorus and arsenic commonly belong to group 5B elements, their anion exchange properties to hydrous zirconium oxide must be similar to each other. In fact acid dissociation constants of phosphoric acid and those of arsenic acid are mutually close.[12] However a detailed description of the adsorption of arsenic on hydrous zirconium oxide has not been reported. In addition, a common drawback of inorganic ion exchangers is the difficulty to obtain spherical beads of suitable size for the required applications. So far we have obtained hydrous metal oxides (M=Zr, Ce) loaded resin by impregnation of metal alkoxide into porous resin beads followed by hydrolysis of the alkoxide[13]. In the present work we have loaded monoclinic hydrous zirconium oxide by incorporation of $ZrOCl_2 \cdot 8H_2O$ into Amberlite XAD-7 followed by hydrolysis of the zirconium compound with ammonia and hydrothermal treatment of the resin. We found that the obtained resin beads (Zr-resin) strongly retained As(III) and As(V). The Zr-resin was applied to the column separation of arsenic ions.

The Zr-resin was prepared by the following procedures: To a solution containing 43.8 g of $ZrOCl_2 \cdot 8H_2O$ in methanol (250 cm^3) was added 35 g of dried Amberlite XAD-7 (specific surface area, 473 m^{2}g^{-1}) and the mixture was placed under reduced pressure. After 30 min, methanol was evaporated off. To the dried residue, 28% ammonia (150 cm^3) was added and the contents stirred for 5 h. Then 500 cm^3 of water was added and the white precipitate so formed was removed by decantation. The pH of resin and water slurry was adjusted to approximately 2.0 and then transferred into a Teflon-lined autoclave for hydrothermal treatment. The autoclave was placed in a furnace and heated at 150 ℃ for 15 h. The resin thus obtained was washed with ethanol and dried (yield, 47.8 g). The resin beads contain 23% of zirconium which corresponds to 2.6 mmol of zirconium per gram of the resin. The specific surface area of this resin is 373 m^{2}g^{-1}.

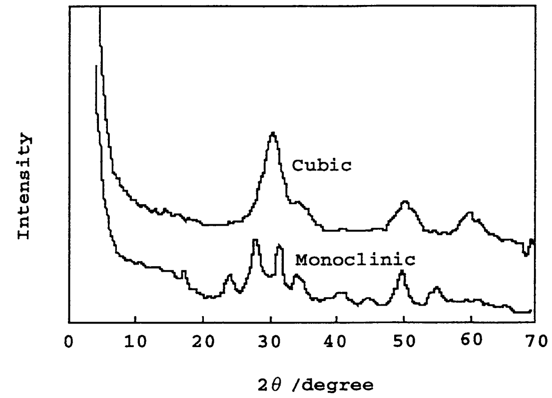

Figure 1. X-ray diffraction patterns of the Zr-resins obtained by the different hydrothermal treatment conditions.
Monoclinic crystals: heated with acidic solution (pH 2) at 150 ℃ for 15 h.
Cubic crystals: Refluxed with 30% NaOH solution for 3h.

Figure 1 shows the X-ray diffraction patterns of the Zr-resin. The zirconium species initially deposited by hydrolysis is an amorphous gel. Obvious crystal growth was observed upon hydrothermal treatment of the resin. Heating the resin in an acidic solution uniquely gave monoclinic crystals while refluxed under basic condition (30% NaOH solution) cubic crystals deposited.[14]

Pore distribution of the Zr-resin (monoclinic) and XAD-7 itself indicated that hydrous zirconium oxide appeared to deposit inside the large size pores since most of the pores of large diameter disappeared remarkably while those less than 40 Å diameter remain unclogged. It was found that a tetrameric complex ion of zirconyl chloride exists in its concentrated solution and upon addition of base such ion tends to polymerize[15]. The sharp distribution of pore diameter of Zr-resin may be attributed to the size restriction of hydrous zirconium oxide gel.

The adsorption properties of the monoclinic Zr-resin for As(III) and As(V) were examined. The analysis of arsenic was carried out with ICP-atomic emission spectrometer. The Zr-resin readily adsorbs As(III) at pH around 9-10 while As(V) is favorably adsorbed at pH from 4 to 6. The adsorption of

As(III) and As(V) is appreciably rapid in the above pH ranges, i.e., equilibrium was attained in at least 6 hours shaking. The maximum adsorption capacities for As(III) and As(V) in batch experiments are around 1.5 and 1.2 mmol g^{-1}, respectively. The distribution coefficient (Kd) defined below was measured under a batchwise procedure.

$$\mathrm{Kd} = \frac{\text{amount of As retained on one gram of resin}}{\text{amount of As remained in 1 cm}^3\text{ of the solution}}$$

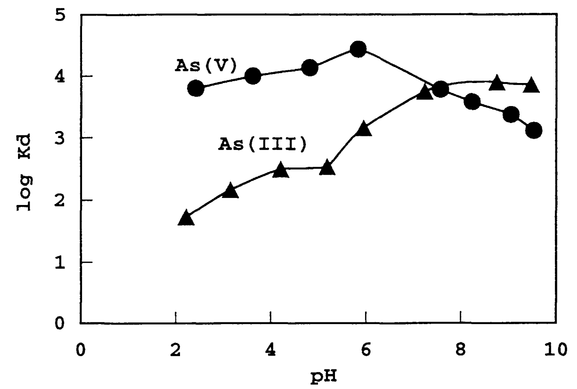

Figure 2. Distribution coefficient (Kd) for the monoclinic Zr-resin as a function of pH.
Resin: 1 g, Initial concentration of arsenic: 1 mM.

Figure 2 shows the log Kd values for As(III) and As(V) as a function of pH. The Kd values of As(III) are rather lower in an acidic region but high at pH neutral to alkaline side, where the distribution of monoanionic species ($H_2AsO_3^-$) is predominant. While the Kd values for As(V) are high in acidic and neutral region and then gradually decrease upon increase of pH. The pKa_1 and pKa_2 for H_3AsO_4 are 2.24 and 6.96, respectively,[15] and therefore the monoanionic $H_2AsO_4^-$ is likely to be responsible for the adsorption species. Appreciably high Kd values at basic region suggest the adsorption of $HAsO_4^{2-}$ in this region. The presence of common anions including Cl^-, NO_3^-, $CH_3CO_2^-$ and SO_4^{2-} did not affect the Kd values for the adsorption of As(V) in the concentration range up to 100 times to that of As(V). Among the anions examined, PO_4^{3-} and F^- are the strongest interferants.

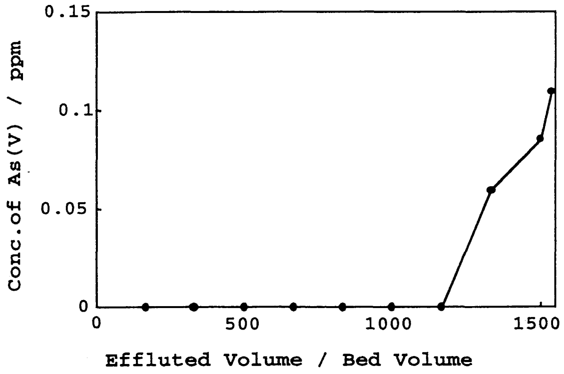

Figure 3. Column breakthrough profile for the adsorption of As(V) by the monoclinic Zr-resin.
Resin bed: 2 g (5.1 cm^3), As(V) feed: 10 ppm, pH: 5.0,
Rate of feed: 0.5 cm^{3}min^{-1}.

Column adsorption of As(V) was examined by using a glass column packed with 2 g of Zr-resin (ϕ 1.0 x 6.7 cm). A buffered solution of pH 5 containing 10 ppm of As(V) was continuously passed through the column at a rate of 0.5 ml min^{-1} (space velocity, 5 beds h^{-1}). The solution out of the column was fractionated and the concentration of As(V) was monitored not to exceed the permission limit of industrial effluent standard, i.e., 0.1 ppm. Figure 3 shows the typical column breakthrough curve. As(V) was favorably retained on the column to allow the passage of the feed solution for more than 1300 times of the bed volume. The concentration of the As(V) ion in the effluent up to 1000 bed volumes was less than the detection limit of ICP-AES. Approximately 35 mg of As was retained on 1 g of the resin at the breakthrough point. The As(V) retained on the column was released from the resin by elution with 1 mol dm^{-3} sodium hydroxide solution. A sharp elution was obtained where more than 98% of the As(V) fed into the column was contained in only 6 times of the bed volume. This corresponds to an enrichment being nearly 200 times relative to initial feed solution. The column was used repeatedly upon washing with water, rinsing with 0.2 mol dm^{-3} acetate buffer (pH 4.2) followed by washing with water. In a similar manner column adsorption of As(III) (10 ppm) was examined at pH 9. In this case 1400 ml of the solution which corresponds to about 400 times of the bed volume can be passed. The leaking of zirconium was practically negligible during the adsorption and regeneration cycles and the column can be used at least 5 times without decreasing the column performance.

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