Highly Effective Removal of Arsenate and Arsenite Ion through Anion Exchange on Zirconium Sulfate-Surfactant Micelle Mesostructure

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The zirconium sulfate-surfactant micelle mesostructure (ZS) works as an excellent anion exchanger to remove arsenic ion in an aqueous solution. The amounts of As trapped in ZS reached to 1.8 mol/mol-Zr.

Of the many toxic metals that may be present as contaminants in natural waters and wastewaters, arsenic is an issue of increasing concern, since arsenic in drinking waters is associated with liver and lung cancers as well as skin cancer.[1,2] The water in India, Southeast Asia, or China contains a high density of arsenic. Arsenic-containing wastewaters are generated during the manufacturing of semiconductor devices. Coprecipitation and adsorption/ion exchange methods have widely been studied to remove arsenic. The former, however, has the disadvantage that a small amount of arsenic ion remains in the solution owing to the solubility of the precipitates. The wet bulky sludge is also the problem. The adsorption or ion exchange of arsenic anion has been studied on various oxides and hydroxides of Fe,[3] Zr,[4] and Y.[5] The capacities of these adsorbents are not so great; that is, all or most of the cations should be efficient for the adsorption/ion exchange of arsenic.

In the study on mesostructured zirconium oxide with regular pore structure, a few research groups found that phosphoric acid treatment can stabilize the pore structure of zirconium sulfate.[6,7] We confirmed the proceeding of novel anion exchange between HSO_4^- in the precursor and $H_2PO_4^-$ in the solution during the treatment.[7] This is an interesting result from the viewpoint that the mesostructured materials containing the surfactant micelles could be used as the very effective anion exchanger.

It is well known that phosphorus and arsenic are both the group 15 elements and the chemical properties of arsenic ion are quite similar to those of phosphorous ion.[8] Thus, this study was designed to investigate the fundamental aspects of a possible remediation strategy for arsenic removal using the mesostructured materials as a new type of anion exchangers.

Hexagonally mesostructured zirconium sulfate (ZS) was synthesized from $Zr(SO_4)_2 \cdot 4H_2O$ and hexadecyltrimethylammonium bromide (C_{16}TMABr, template) by the procedure reported previously.[7] The samples were characterized with XRD, TEM, ICP, and elemental analysis. The ZS powders showed characteristic (100), (110), and (200) XRD diffractions of the hexagonal structure with d spacings of 4.28–4.06, 2.47–2.36, and 2.17–2.03 nm. The chemical formula was $Zr(HSO_4)(OH)_{3.5}(C_{19}H_{42}N)_{0.5} \cdot 2H_2O$.

In the typical ion exchange experiments, 0.01 g of ZS was added into a solution of 100 ml containing 50 ppb–1000 ppm of arsenic ion at various pH. The equilibrium values of pH and the amounts of arsenic removed were determined after 18 or 36 h of ion exchange unless otherwise stated. The concentration of arsenic ion was determined by a polarizing Zeeman-effect atomic absorption spectrophotometer. The distribution coefficient K_d was defined as $K_d = M_r/M_s$, where M_r and M_s were the respective amounts of arsenic ion exchanged into one gram of the ion exchanger and remaining in one ml of the solution.

At first the kinetics of the ion exchanges is summarized in Figure 1. The reaction of arsenate ion was very rapid and an approximate equilibrium could be attained within 20 min. In contrast the reaction of arsenite ion proceeded slowly. We could get the equilibrium after 36 h. The results well coincide with those on basic yttrium carbonate,[5] though the reason for the great difference between the reaction rates of arsenate and arsenite ions is unclear at the present.

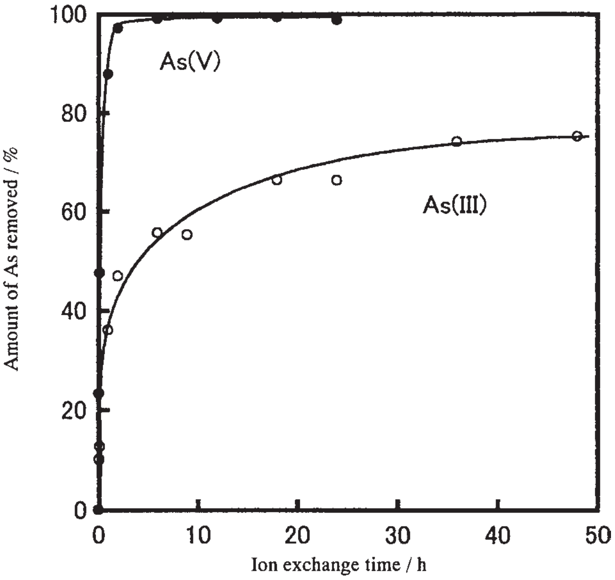

Figure 1. Ion exchange kinetics of arsenate (●) and arsenite (○) on the ZS powder. Reaction conditions: 10 mg of ZS, 60 ml of aqueous solution, 5 ppm of As, at 303 K, and 7.5 (As^{5+}) and 10.0 (As^{3+}) of initial pH.

The isotherm of sorption of arsenate ion on the ZS powders is shown in Figure 2. The literature data[9] are also plotted in the same figure for comparison. One can recognize that ZS has an excellent ability for the sorption of arsenate ion: The amount of As sorbed on ZS sharply increased at very low As concentration, and was much greater than those on activated carbon, alumina, and rare-earth compounds reported so far. The ion exchange isotherm on ZS could be analyzed by using the Langmuir equation, where there are some assumptions that there is equilibrium of arsenic ion between the aqueous and solid phases and the affinity of arsenic ion for the ion exchanger is uniform. The saturated sorption capacity of arsenate ion was calculated to be 3.06 mmol g-ZS^{-1}

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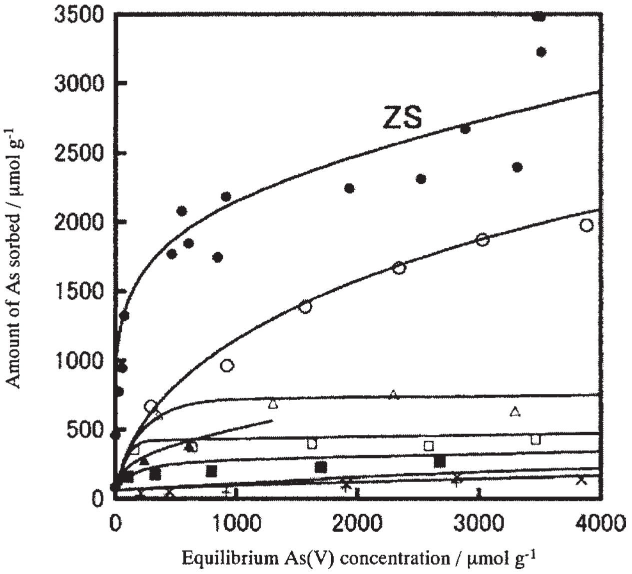

Figure 2. As sorption isotherms on various absorbents and ion exchangers. ZS (●), lanthanum hydroxide (○), lanthanum carbonate (△), basic lanthanum carbonate (▲), active alumina A (□), active alumina B (■), activated carbon A (×), and activated carbon B (+).

(= 1.8 mol/mol-Zr) at pH 4.5 and 303 K. That of arsenite was 2.81 at 9.5 and 303 K. These values are much greater than those on the other adsorbents.

Figure 3 shows the K_d values of arsenate and arsenite ion as a function of pH. The maximum log K_d of arsenate ion was observed at pH 3.8–4.5 and reached approximately 5. It is already reported that arsenate species exist as oxoanions in an aqueous solution, which are depicted at top of the figure.[10] At pH 3.0–6.5, the predominant species is $H_2AsO_4^-$. One can suggest that this monoanion species would be active for the ion exchange. On the other hand, the maximum log K_d value, 4.3, of arsenite ion was obtained at pH of 9.0–9.5 and was lower than the value of arsenate. At this pH region the predominant species is $H_2AsO_3^-$ monoanion.[10] It is again suggested that the monoanion species would be active in the ion exchange.

Changes in the mesostructure and the composition of ZS before and after the ion exchange treatment were examined. The XRD diffraction patterns after the ion exchange were almost the same as those of the fresh sample, indicating no collapse of the hexagonal structure. The (100) diffractions, however, were observed at $d = 4.18$–4.01 nm, which were somewhat smaller than the original one and suggest small shrinking of the lattice. It was further found that the filtrate after the ion exchange treatment contained small amounts of surfactant and Zr ion other than much amount of sulfate ion. They were equivalent to ca. 3 wt% ZS. This means the partial dissolution of ZS in the present ion exchange treatment.

The influence of the coexisting anions on the ion exchange of arsenate ion (5 ppm) was studied. The presence of Cl^-, F^-, NO_3^-, and SO_4^{2-} did not interfere with the ion exchange when their concentrations were lower than 100 ppm. $H_2PO_4^-$ showed high affinity to ZS and was the strong interferant. At last it would be worthy to note that washing of the As-sorbed ZS powders with a sulfuric acid solution (0.9 M) resulted in the desorption of about half of arsenic ion loaded and the reintroduction of sulfate ion.

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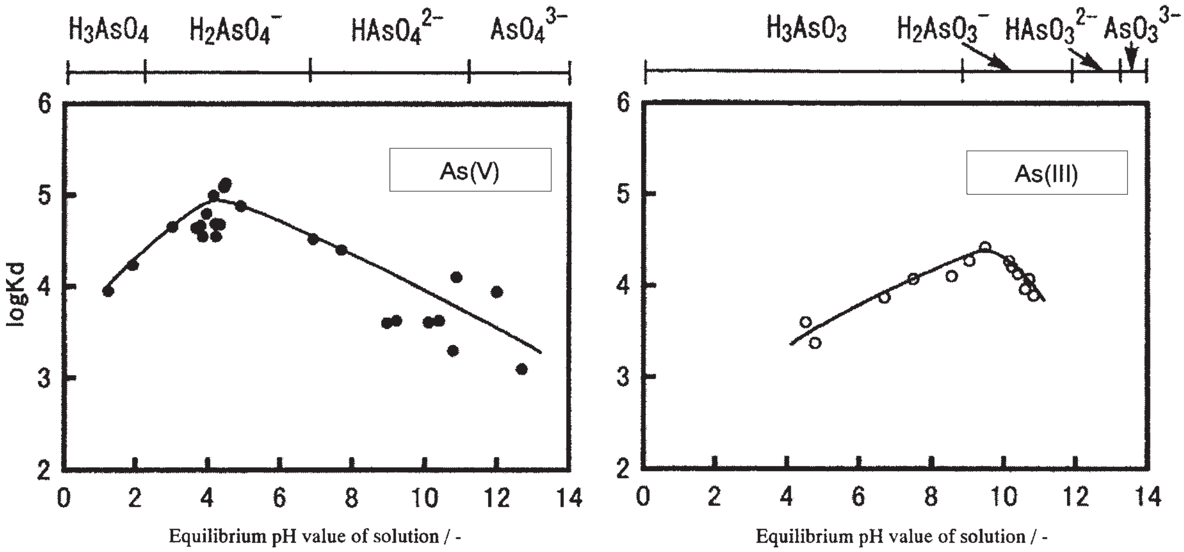

Figure 3. Change in distribution coefficient (K_d) of arsenate and arsenite ion on ZS with the equilibrium pH of solution. Reaction conditions: 6 mg of ZS, 60 ml of solution, approximately 5 ppm of initial conc. of As, at 303 K, and 18 (As^{5+}) or 36 h (As^{3+}) of sorption time.