Zirconium Sulfate–Surfactant Micelle Mesostructure as an Effective Remover of Selenite Ion

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Selenite ion in an aqueous solution could be effectively trapped in the zirconium sulfate–surfactant micelle mesostructure (ZS). The reaction proceeded through anion exchange between HSO_4^- in ZS and $HSeO_3^-$. The maximum sorption capacity of ZS for $HSeO_3^-$ was 2.47 mmol g^{-1} at 303 K.

Although selenium is an essential element in animals and plants, its too much dosage is toxic, resulting in skin diseases. The maximum concentration of selenium in drinking water in Japan is 0.01 mg/L. Selenium is mainly used as additives in catalysts, insecticides, and semiconductors. The effluents from these industries contain selenium in high concentrations as well as those from copper industries and oil refineries. In addition, the treatment of selenium used as photovoltaic devices in copy machines until recently is also the problem to be solved. The major selenium species in such wastewaters are Se(IV) and Se(VI) oxyanions. The former should be preferentially removed from the waters since the toxicity of Se(IV) is higher than that of Se(VI) and the predominant species in the wastewaters is usually Se(IV).[1] Precipitation method is not so effective because of the high solubility of selenium oxyanions. Many attempts, therefore, have been made to adsorb selenite and a lot of adsorbents such as goethite,[2] hydrous titanium dioxide,[3] and γ-alumina[4] have been suggested as effective adsorbents.

The hexagonally mesostructured zirconium sulfate–surfactant micelle (ZS) has regular array of surfactant micelles and contains sulfate ion (HSO_4^-) in its wall. This sulfate ion can be ion-exchanged with the other type of anions such as phosphate ion and arsenic ion in aqueous solutions, as has already been reported.[5,6] Thus we have expected that ZS would be a good/excellent anion exchanger for selenite ion. In the present study, we would show that ZS can remove selenite effectively and the exchange of selenite and sulfate ions proceeds with 1:1 ratio.

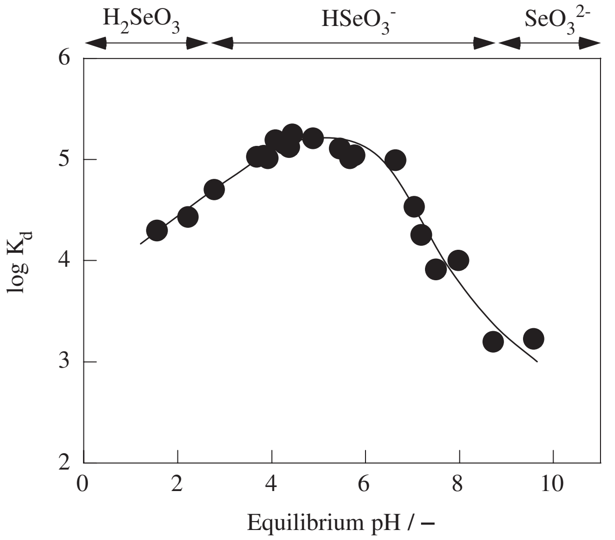

Figure 1. Change in K_d with pH of solution. 6 ppm of initial concentration of Se, 6 mg of ZS, at 303 K and 24 h shaking.

ZS was synthesized by the procedure reported in previous papers.[5–7] The chemical composition of obtained ZS was $Zr(HSO_4)\cdot(C_{19}H_{42}N)_{0.5}(OH)_{3.5}\cdot 2H_2O$.[5] The selenium removal experiments were carried out by using aqueous solutions of H_2SeO_3 (Se(IV)). It is reported in a few papers that the sorption capacity is dependent on the coexisting ions in the solution,[4] but in the present study all experiments were performed without any addition of the other kinds of salts. Unless otherwise stated, ZS was added into 60 ml of a pH-controlled selenium solution where the pH value was adjusted by adding an aqueous ammonia or HCl solution. The solution was shaken at 303 K for 24 h. After the filtration, the concentrations of Zr and Se in the filtrate and the recovered ZS were determined by ICP. The amount of S was measured by elemental analysis.

Figure 1 shows the pH dependence of the amount of selenium introduced into ZS. The pH values measured after 24 h ion exchange (equilibrium pH) are plotted as abscissa. The distribution constant, K_d was defined as $K_d = M_r/M_s$, where M_r and M_s were the respective amounts of selenium exchanged into one gram of ZS and remaining in 1 mL of the solution. The highest K_d value was obtained at pH 4.0–6.0. The predominant ion species of Se(IV) in the pH range 2.5–8.0 is the monovalent anion $HSeO_3^-$. It follows that effective removal of selenite with ZS would proceed in the presence of $HSeO_3^-$ monoanion.

The isotherm of Se(IV) ion exchange on ZS at 303 K is

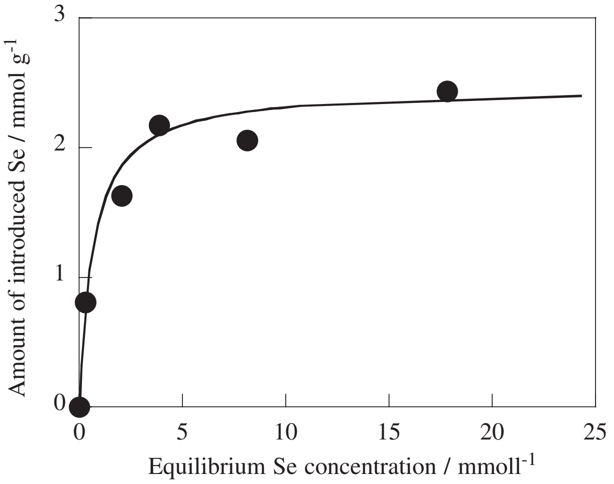

Figure 2. Selenite removal isotherm at 303 K. Initial concentration of Se: 3–30 mmol L^{-1}, ZS: 0.1–0.3 g.

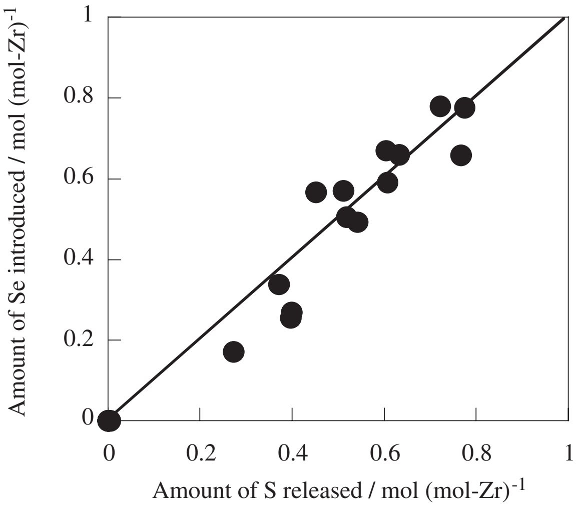

Figure 3. Correlation between amounts of Se introduced into and S released from ZS. The solid line shows the 1:1 ratio of the amounts of Se introduced and S released.

shown in Figure 2. Initial pH values of solutions were adjusted at 7.15–8.89, because the pH values always decreased by the release of HSO_4^- during the ion exchange. The maximum selenium sorption capacity (W_s) and Langmuir constant (K) of Se(IV) was 2.47 mmol g^{-1} and 1.49 l mmol^{-1}, respectively. To the best of our knowledge, the largest sorption capacities, W_s, have been reported on γ-alumina[4] and titania,[3] which are 1.97 and 2.0 mmol g^{-1}, respectively. The value observed on ZS, 2.47, is clearly greater than these values. This value is also much higher than 0.38 reported on Zr-loading resin.[8]

To confirm the anion-exchange mechanism, the correlation between the amounts of S released from and Se(IV) introduced into ZS was examined and summarized in Figure 3. The linear line is drawn for the 1:1 relationship between them. All of the experimental data fell on the line within experimental error, indicating the 1:1 ion-exchange reaction.

Selenite ion introduced into ZS was characterized by FTIR. Figure 4a depicts FTIR spectra of ZS treated in the Se solutions. The difference spectra, based on the spectrum (a), are also shown in Figure 4b. The intensity of the peaks at 860, 750, and 640 cm^{-1}, which can be attributed to the Se species $HSeO_3^-$,[9] increased with increasing Se/Zr ratio in ZS. On the other hand, the peak intensity at 1000–1300 and 640–610 cm^{-1} attributable to HSO_4^- ion[10] decreased. It follows that the selenium ion species, $HSeO_3^-$, is introduced into ZS through the ion exchange with HSO_4^-.

$$HSeO_3^-{}_{(s)} + HSO_4^-{}_{(ZS)} \rightarrow HSeO_3^-{}_{(ZS)} + HSO_4^-{}_{(s)}$$

In this reaction, the subscripts (s) and (ZS) denote the species existing in aqueous solution and in ZS, respectively. This exchange reaction is quite different from that for the arsenate ion removal with ZS.[5]

$$\begin{aligned} &H_2AsO_4^-{}_{(s)} + HSO_4^-{}_{(ZS)} + 2OH^-{}_{(ZS)} \\ &\quad \rightarrow AsO_4^{3-}{}_{(ZS)} + HSO_4^-{}_{(s)} + 2H_2O_{(s)} \end{aligned}$$

The As ion species was introduced as AsO_4^{3-} with releasing two OH^- anions. The reason of this difference should be clarified in the near future.

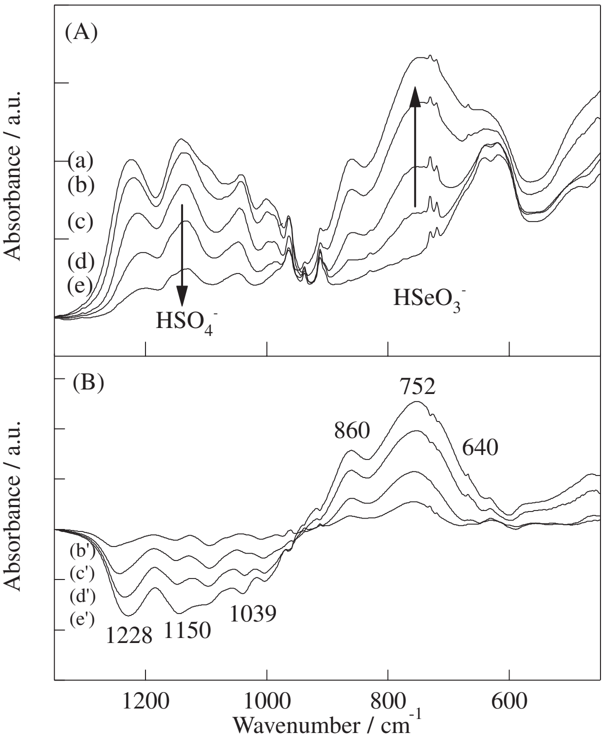

Figure 4. FTIR spectra (A) and difference spectra (B) of ZS treated in Se solutions. Se/Zr ratio: (a) 0.00, (b) 0.11, (c) 0.35, (d) 0.66, and (e) 0.78. In difference spectra, (b′) (b)–(a), (c′) (c)–(a), (d′) (d)–(a), and (e′) (e)–(a).

At last two findings should be noted. First, little change in the XRD peaks of ion exchanged ZS confirmed the stability of ZS during the ion exchange treatments, but the lattice constant slightly decreased from 4.737 to 4.440 nm by the treatment at initial pH 7.77. Second, 1.2–2.2 ng of Zr leached out from 0.1 g of ZS (containing 23.7 mg of Zr) during the experiment. This also concluded the high stability of ZS. ZS could be employed as highly effective remover of selenite from industrial wastewaters or polluted soils.

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