Behavior of Iminodiacetate Fiber in Column-mode Adsorption of Lead(II)

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Abstract
Chloromethylstyrene-grafted polyethylene-coated polypropylene fiber (0.9 denier, length
3.7 cm) was functionalized by reaction with diethyl iminodiacetate and subsequent
hydrolysis of the ester introduced. An acid capacity of the resulting chelating fiber
(FIDA-f) was 4.3 meq/g. Although a maximum permissible flow rate of feeds was
depressed with an increase in the conditioning pH of the FIDA-f column, breakthrough
profiles of Pb(II) were independent of the flow rate of feeds up to 800 h\(^{-1}\) in space velocity
(SV). The usefulness of FIDA-f was demonstrated by quantitative removal of Pb(II) from
600 bed volumes of a Pb(II)-spiked river water (5 ppm) at a flow rate of SV 400 h\(^{-1}\).

1 Introduction
Although iminodiacetate resins are the most widely used chelating resins, one of their disadvantages is
slow kinetics in the adsorption of metal ions.[1] In order to obtain iminodiacetate chelating exchangers with high
kinetic performances, fibrous exchangers with iminodiacetate groups have been studied from the end of 1960’s.
[1-3] At present, few iminodiacetic acid fibers are already commercially available.[1,3] However, there is still
room to improve adsorption rates of these chelating fibers. In this connection, we have recently identified that
phosphonylation of chloromethylstyrene-grafted polyethylene-coated polypropylene fibers (FCMS-f) gave
phosphonate cation exchange fibers with extremely rapid adsorption rates of heavy metal ions.[4] Therefore, it is
expected that an iminodiacetate fiber FIDA-f derived from FCMS-f will also exhibits extremely rapid rates in
uptake of heavy metal ions. In this work, FIDA-f was prepared from FCMS-f and its kinetic performances in
uptake of Pb(II) were investigated by means of a columnar method.

2 Experimental
2.1 Materials
Polyethylene coated polypropylene filamentary fiber (PPPE-f, 0.9 denier, length ca. 3.8 cm) was
provided by Kurashiki Textile MFG Co., Osaka, Japan, and chloromethylstyrene (CMS) by Seimi chemical Co.,
Chigasaki, Japan. Method of graft polymerization of CMS onto PPPE-f was reported in detail elsewhere.[4] The
amount of grafted CMS in the resulting CMS grafted fiber (FCMS-f) was 1.07 g/g of PPPE-f. Other reagents
were of reagent grade, unless otherwise specified.

2.2 Functionalization of FCMS-f

FCMS-f (0.5g) was heated with a mixture of diethyl iminodiacetate (9 cm³) and ethanol (6 cm³) at 120 °C for 3 h in a stainless steel autoclave. Amounts of introduced diethyl iminodiacetate in the resulting fiber were 2.12 ± 0.02 mmol/g for three separate syntheses, and the hydrolysis of the introduced diethyl iminodiacetate was carried out by heating the resulting fiber in 1 M (M = mol dm⁻³) NaOH (150 cm³) under reflux for 9 h. After the hydrolysis reaction, the resulting chelating fiber FIDA-f was treated with 1 M hydrochloric acid, and then equilibrated with dilute hydrochloric acid (pH 2). The FIDA-f in the hydrogen ion form was air-dried and then dried in vacuum at 40 °C for 24 h. Acid capacities of FIDA-f prepared three separate runs were 4.28 ± 0.03 meq/g, which are nearly equal to ones estimated from the nitrogen contents mentioned above.

2.3 Preparation of FIDA-f packed columns

After the hydrogen ion form FIDA-f (0.50 g) was swollen in 1 M CH₃COONa for 24 h, it was packed into a glass column (i.d. 0.90 cm); this column named C-a, and its wet bed volumes in the column C-a were measured under different conditions. In order to study effects of amount of FIDA-f and diameters of columns on breakthrough profiles of Pb(II), an alternative glass column named C-b (i.d. 0.70 cm) was packed with the hydrogen ion form FIDA-f (0.40 g), and was equilibrated with a dilute hydrochloric acid of pH 2. After the three times adsorption and elution cycles of Pb(II), the FIDA-f in the column C-b was transferred into the column C-c (i.d. 0.96 cm) to investigate breakthrough profiles of Pb(II) in the wide range of feed flow rate.

2.4 Column mode adsorption and elution of Pb(II)

After each column was equilibrated with an acetic acid/sodium acetate buffer of pH 4.6 - 4.7 (0.1 M of each), a loading solution containing Pb(II) was fed to the column at various flow rates. Washing the column with water, metal ions adsorbed were eluted with 1 M HNO₃. After washing the column with water, the column was equilibrated again with the acetic acid/sodium acetate buffer for the next adsorption operation. Effluents including washings were collected on a fraction collector, and concentrations of metal ions in each fractions were determined by means of ICP-AES. Flow rates of feeds were controlled by a peristaltic pump placed at downstream of a column. Flow rates of eluent and water were fixed at a given flow rate. Breakthrough points of metal ions were designated as the volume of feed corresponding to C/C₀ = 0.05; here C₀ and C are concentrations of a metal ion in the feed and column effluent, respectively. Detailed experimental conditions will be given with results in later sections.

3 Results and Discussion

3.1 Swelling Behavior of FIDA-f

Table 1 summarizes wet bed volumes of FIDA-f in the column C-a after contacting various solutions and water as well. After contact with 1 M sodium acetate, FIDA-f exhibits the largest volume of 6.2 cm³. Since the second proton of the fixed functional groups is neutralized at ca. pH 9,[5] FIDA-f highly swells in 1 M CH₃COONa. However, the volume of FIDA-f decreased down to 2.9 cm³ after contact with the buffer of pH 4.6. The smallest wet volume of 2.5 cm³ was observed after contact with 1 M nitric acid. Table 1 suggests that the change in the wet volume of FIDA-f is
not significant below pH 6.

3.2 Behavior of FIDA-f Pretreated with 1 M CH₃COONa in Column-mode Adsorption of Pb(II)

Figure 1 shows breakthrough profiles of Pb(II) during supply of the feed containing Pb(II) of 10 mM to the column C-a. Shapes of breakthrough curves of Pb(II) are essentially independent of flow rates of the feed up to the flow rate of 600 cm³/h, which nearly corresponds to an hourly flow rate of 200 bed volumes so long as the fiber bed volume of 2.9 cm³ just before the adsorption operation was adopted as the reference bed volume to convert the flow rate in cm³/h into space velocity in h⁻¹. The breakthrough and column capacities are 1.4 - 1.5 and 1.9 - 2.1 mmol/g, respectively. Adsorbed Pb(II) was quantitatively eluted with 1 M nitric acid.

Since Ca(II) and Mg(II) are the main divalent cations in natural water, their effects on the adsorption of Pb(II) were studied by supplying solutions containing Pb(II)-Ca(II) or Pb(II)-Mg(II) to the column Ga. Figure 2 illustratively shows breakthrough profiles of both Pb(II) and Ca(II) in the adsorption operations. Both profiles are almost independent of flow rates of the feed. Values of C/Co for Ca(II) exceed unity between about 70 and 200 cm³ of the feed. This means that less preferred Ca(II) adsorbed at the beginning of the adsorption operation was eluted by more preferred Pb(II). Because of flow rate independent profiles of both Pb(II) and Ca(II), the cation exchange reaction between the adsorbed Ca(II) on the fiber with Pb(II) in the solution is also extremely rapid. For Pb(II)-Mg(II) binary system, almost the same results were observed. Breakthrough and column capacities for Pb(II) in the binary systems are 1.4 - 1.6 and 1.7 - 1.8 meq/g, respectively. In the nitric acid eluates, Ca(II) and Mg(II) were not detected, indicating that they were completely substituted with more preferred Pb(II) so long as the equilibrium was established between the FIDA-f and the feed. Thus, it is expected that FIDA-f is promising in the selective and rapid removal of Pb(II) from Pb(II)-polluted natural water.

3.3 Comparison of Breakthrough Capacities of FIDA-f among Three Columns

The smooth supply of the feed was difficult to achieve above 600 cm³/h in the case of the column C-a, and then the column C-b was prepared by packing 0.4 g of FIDA-f into a glass column (i.d. 0.70 cm). After equilibration of the column C-b with a dilute hydrochloric acid of pH 2, the volume and height of the wet FIDA-f bed became 1.7 cm³ and 4.3 cm, respectively. After equilibration of this column with acetic acid/sodium acetate buffer of pH 4.7, the adsorption capacity of Pb(II) was determined. The results are shown in Figure 3.
operation of Pb(II) was conducted at two different flow rates of 330 and 660 cm$^3$/h. Figure 3 shows the results; here, the results for the column C-a are also shown for comparison. Although the column C-b gives flow rate independent breakthrough profiles of Pb(II) up to 660 cm$^3$/h, breakthrough capacities for Pb(II) of this column per unit weight of FIDA-f were slightly lower than that of the column C-a, and further increase in flow rate was difficult in the case of the column C-b, too. Then, FIDA-f in the column C-b was transferred into the column C-c (i.d. 0.96 cm) in order to lower the resistance for high flow rates of the feed. As shown in Fig. 3, the column C-c also gave the flow rate independent breakthrough profiles, whereas breakthrough capacities of the column C-c were further lowered. Breakthrough capacities of three columns for Pb(II) per unit weight of FIDA-f are summarized in Table 2. Although breakthrough profiles and capacities are affected by geometries of columns, amounts of packed FIDA-f, and pretreatment methods of FIDA-f, column capacities per unit weight of FIDA-f were almost constant; average of column capacities for 16 runs shown in Table 2 is 2.08 ± 0.10 mmol/g. It seems that the treatment of FIDA-f with 1 M CH$_3$COONa improves its kinetic performances. However, more detailed studies must be required to explain these interesting phenomena. At present stage, we would like to only point out that the column C-c is able to give satisfactory breakthrough capacities of ca. 0.7 mmol/g for Pb(II) at the extremely high flow rate of 1300 cm$^3$/h, which corresponds to ca. 800 h$^{-1}$ in space velocity.

3.4 Removal of Pb(II) from Pb(In Spiked River Water)

The removal of Pb(II) from a simulated natural water sample contaminated with Pb(II) was tested to judge practical usefulness of FIDA-f. The simulated sample was prepared by spiking Pb(II) to river water sample collected from Shirakawa river (Kumamoto-shi, Japan). The sampled water was left to sediment for one day, it was filtered with filter paper. The pH value was adjusted to 5 with nitric acid to avoid precipitation of spiked Pb(II) as hydroxide. Then, lead nitrate was spiked and the final concentration of Pb(II) of the resulting sample was 5 ppm. This simulated sample (0.99 L) was supplied to the column C-c at the flow rate of 660 cm$^3$/h (ca. 400 h$^{-1}$ in space velocity). This column quantitatively removed Pb(II) from the simulated sample. Thus, only 0.4 g of dried FIDA-f (ca. 1.7 cm$^3$ of wet FIDA-f) was able to purify ca. 600 bed volumes of the Pb(II)-contaminated water sample within 1.5 h. As demonstrated here, FIDA-f is useful for rapid purification of huge volumes of water contaminated with ppm levels of Pb(II).

References