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Sorption Properties and Some Separations of Divalent Transition Metal Ions on Crystalline Hydrous Titanium Dioxide Fibers

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Abstract

The sorption of some divalent transition metal ions and strontium ion on crystalline hydrous titanium dioxide fibers has been studied. Crystalline hydrous titanium dioxide fibers were obtained by extracting potassium ions from potassium tetratitanate ($K_2Ti_4O_9$) fibers; their composition was $TiO_2 \cdot 0.6H_2O$. It was confirmed that these metal ions were sorbed on this material by an ion-exchange reaction, and their selectivity series $Cu > Sr > Zn > Mn > Co > Ni$ was established. Large separation factors were obtained between copper ion and other divalent transition metal ions, and some mutual separations have been achieved on a column containing crystalline hydrous titanium dioxide fibers.

INTRODUCTION

Hydrous titanium dioxide is one of the inorganic ion-exchangers that have attracted considerable attention because this material has a high sorption selectivity for certain metal ions. Many papers have presented the basic characters and sorption properties of this material (*1–6*). This material has been also studied as the selective sorbent of uranyl ion from seawater (*7,8*). On the other hand, it has been reported that this material can advantageously be used for the treatment of high-level radwaste elements (*9*). Three types of hydrous titanium dioxide have been reported so far: amorphous, anatase-type, and rutile-type hydrous titanium dioxide (*5*). But the crystallinities of these materials are poor and they are not suitable for column operations owing to their fine particle size.

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In 1980, Ohta and Fujiki reported a new type of hydrous titanium dioxide, named crystalline hydrous titanium dioxide fibers, as the derivative of potassium tetratitanate ($K_2Ti_4O_9$) fibers (*10, 11*). Because this material is crystalline and has a fiber form, it is very suitable for column operations. By using this material as an ion-sorbent, Fujiki et al. proposed immobilization processes of cesium and strontium ions in aqueous solutions from the viewpoint of high-level radwaste treatment (*12, 13*). They have also studied the basic characteristics of this material as an inorganic ion-exchanger, and report that cesium ion can be sorbed selectively among alkali metal ions (*14, 15*).

This paper describes the sorption properties of crystalline hydrous titanium dioxide fibers for divalent transition metal ions as well as for strontium ion. Some mutual separations of copper ion from other divalent transition metal ions are also presented.

EXPERIMENTAL

Reagents

All chemicals used were of analytical grade. Distilled, deionized water was used throughout. The solutions of transition metal ions and strontium ion were prepared by dissolving the corresponding nitrate salts with water.

Preparation of Crystalline Hydrous Titanium Dioxide Fibers

Crystalline hydrous titanium dioxide fibers were prepared as follows: potassium tetratitanate ($K_2Ti_4O_9$) fibers were grown from a K_2MoO_4 flux melt containing a mixture of K_2CO_3 and TiO_2 (1:3 molar ratio). To obtain the H^+-form, about 15 g of potassium tetratitanate fibers was placed in a column (2.5 cm i.d.) and 1 mol/dm^3 hydrochloric acid was passed through this column until the potassium ion in the effluent was negligible. Next, distilled, deionized water was passed through this column until the pH of the effluent was 5–6. The resulting product was air-dried to constant weight.

Equilibrium Studies

The equilibrations were carried out batchwise: 0.1 g of sample was treated with 10 mL of solution containing divalent transition metal ions or strontium ion at various pH values or concentrations. The mixtures were shaken intermittently at 30 ± 1°C. After equilibrium was attained, the supernatant solutions were analyzed for their pH value and metal ion content. The distribution coefficient values (K_d) were calculated by using

$$K_d = \frac{\text{moles of metal ion per 1 g of solid}}{\text{moles of metal ion per 1 mL of solution}} (\text{mL/g})$$

Concentrations of metal ions in solid were calculated from the differences between the initial and final concentrations of the aqueous phase. Separation factors (α_A^B) were determined by using

$$\alpha_A^B = K_d^B / K_d^A$$

where K_d^A and K_d^B are the distribution coefficient values of A and B ions.

Apparatus

An AA-875 Varian Atomic Absorption Spectrophotometer was used for determination of the metal ion content in an aqueous phase. A Model HM-20E TOA pH meter was used for all pH measurements. X-ray powder diffraction patterns were taken using a Rigaku Denki Diffractometer with Cu-Kα radiation.

Separation of Copper Ion from Other Divalent Transition Metal Ions

Mutual separations were carried out in a column (1.0 cm i.d.) containing 1.0 g of crystalline hydrous titanium dioxide fibers. A solution containing copper ions and another metal ion (2 μmol each) was loaded into the column and elution began after 1 h by nitric acid at a flow rate of 0.3 mL/min. The effluent fractions were analyzed for their metal ion content.

RESULTS AND DISCUSSION

Characterization of the Sorbent

The extraction of potassium ions from potassium tetratitanate ($K_2Ti_4O_9$) fibers was carried out by a column technique. After passing through 10 dm^3

of 1 mol/dm^3 hydrochloric acid, the potassium ion concentration in the effluent became 1×10^{-5} mol/dm^3 or less. To examine the degree of potassium ion removal at this stage, the resulting product was dissolved by concentrated sulfuric acid and ammonium sulfate with heating, and the potassium ion content was measured by atomic absorption spectrophotometry. The potassium ion content was found to be 1.02 mg/g sorbent, and it was confirmed that almost all potassium ions were removed. The water loss of this product at 600°C was 11.49%. Therefore, the composition of this material can be written as $TiO_2 \cdot 0.6H_2O$.

This product had a fiber form with white color. The fiber size was 1 mm length × 0.01 mm diameter on average.

X-ray powder diffraction pattern showed good agreement with previously reported data (*10*). The strongest reflection was observed at a 2θ value of 9.8°, and several weak reflections appeared above 10°. It is known that this material is crystalline with a layer structure which resembles the layer structure of potassium tetratitanate (*10*).

Sorption Studies

Figure 1 shows the time dependence of sorption of the divalent transition metal ions. 10–14 days were required to attain equilibrium for these metal ions. Thus all the experiments described below were carried out by treating the solid with the metal ion solution for 14 d.

Table 1 gives the distribution coefficient values for various initial concentrations of metal ions. From this table, a selectivity series Cu > Sr > Zn > Mn > Co > Ni can be established on crystalline hydrous titanium dioxide fibers. On the other hand, Abe et al. (*6*) have reported the selectivity series Cu > Zn > Mn > Ni > Co for the amorphous and Cu > Zn > Mn > Co > Ni for the anatase-type hydrous titanium dioxide, which coincides roughly with our data. The distribution coefficient values they reported were almost of the same order as our data. However, Heitner-Wirguin et al. (*3*) have reported considerably larger distribution coefficient values for the amorphous material. They have also reported the selectivity series Co > Ni > Cu, which is very different from our data. It should be pointed out that the sorption properties on hydrous titanium dioxide are strongly dependent on the method of preparation.

Figure 2 shows the distribution coefficient values at various pH values of the aqueous phase with a constant load of metal ions. The acidity was controlled with nitric acid. Plots of log K_d show a good linear relationships with pH values. The values of their slopes were 2.04 for Ni, 1.99 for Co, 1.98 for Mn, 1.90 for Zn, 2.00 for Sr, and 2.19 for Cu, which are

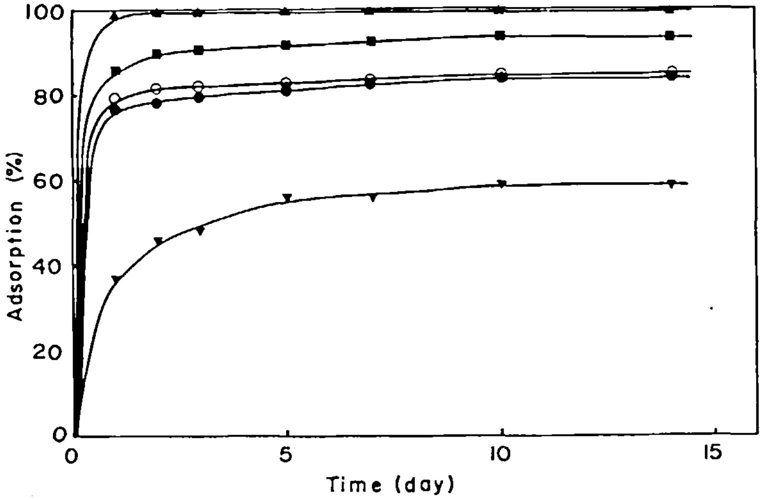

FIG. 1. Time dependence of sorption of transition metal ions. Initial concentration: 1 × 10^{-4} *M*. Initial pH: 4.5–5.5, Cu (▲), Zn (■), Mn (○), Co (●), Ni (▼).

TABLE 1

Distribution Coefficient Values (K_d) on Crystalline Hydrous Titanium Dioxide Fibers[a]

Concentration (*M*)	Cu	Sr	Zn	Mn	Co	Ni
1×10^{-2}	21.4	15.9	—	—	—	—
5×10^{-3}	56.5	22.9	19.5	13.2	8.3	—
2×10^{-3}	298	62.9	33.9	30.2	31.0	—
1×10^{-3}	826	125	58.0	50.2	44.8	11.2
5×10^{-4}	2070	304	108	85.0	81.0	23.2
2×10^{-4}	~10^4	1150	332	233	216	65.6
1×10^{-4}	>10^4	~4000	1300	567	521	139

[a] Initial pH: 4.5–5.5. A dash denotes that the distribution coefficient value was too small to be determined.

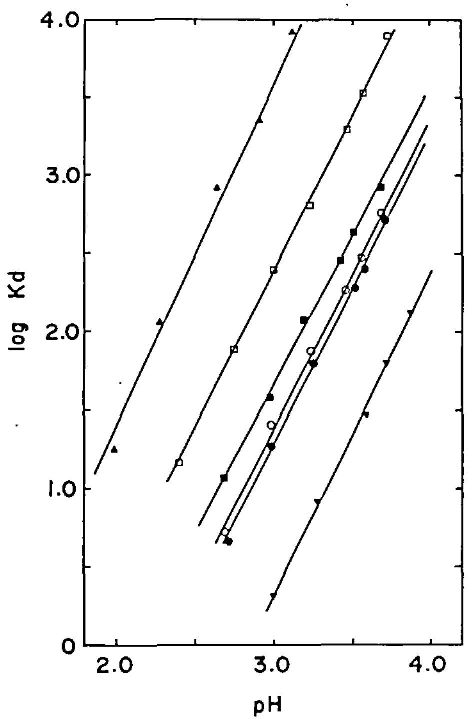

FIG. 2. pH dependence of distribution coefficient values (K_d). Initial concentration: 1 × 10^{-4} *M*. Cu (▲), Sr (□), Zn (■), Mn (○), Co (●), Ni (▼).

approximately equal to the charge of the metal ions studied here. From these results it can be concluded that the sorption of these metal ions on crystalline hydrous titanium dioxide fibers takes place according to the following ion-exchange reaction:

$$H_2R + M^{2+} \rightleftharpoons M{-}R + 2H^+$$

where H_2R and M^{2+} represent the sorbent and metal ion, respectively.

Table 2 gives the values of the distribution coefficient and the separation factor for these metal ions at pH = 3.0. Large separation factors were obtained comparing with those of organic ion-exchange resins (*16*) and other inorganic ion-exchangers such as zirconium phosphate (*17, 18*) and hydrous

TABLE 2

Values of Distribution Coefficient (K_d) and Separation Factor (α_A^B) for Neighboring Ions at pH = 3.0

	Ions										
	Cu		Sr		Zn		Mn		Co		Ni
K_d	3630		240		46		24		19		2.1
α_A^B		15.1		5.2		1.9		1.3		9.0	

titanium dioxide (*6*). This phenomenon may be due to the fact that crystalline hydrous titanium dioxide fibers are crystalline with a layer structure.

Separation of Copper Ion from Other Divalent Transition Metal Ions

Crystalline hydrous titanium dioxide fibers are very suitable for column operations owing to their fiber form. As shown in Table 2, considerably large separation factors were obtained between copper ion and other divalent transition metal ions. Thus some mutual separations between them were attempted by using the column with this material. Figure 3 shows the results of attempted separations of Cu from (a) Zn, (b) Mn, (c) Co, and (d) Ni. 0.5 and 0.001 mol/dm^3 nitric acid were chosen as the eluents for copper ion and other metal ions, respectively. If nitric acid with a concentration larger than 0.001 mol/dm^3 was used as the eluent for the latter, copper ion leaked through the column and resulted in contamination.

In the case of Zn–Cu separation, shown in Fig. 3a, only 75% of Zn loaded was eluted even after 100 mL of 0.001 mol/dm^3 nitric acid was passed through the column. The remaining Zu was eluted with the elution of Cu by 0.5 mol/cm^3 nitric acid, and mutual contamination occurred. This may be due to the fact that the separation factor between Zn and Cu is the smallest of those studied here.

On the other hand, complete separations were achieved for Mn–Cu (Fig. 3b), Co–Cu (Fig. 3c), and Ni–Cu (Fig. 3d), although the elution peaks of the copper ion had a tailing rear. In these cases, 90–95% of the Cu loaded was eluted up to 100 mL of 0.5 mol/dm^3 nitric acid. Almost all copper ions could be eluted by another 50 mL of 0.5 mol/dm^3 nitric acid.

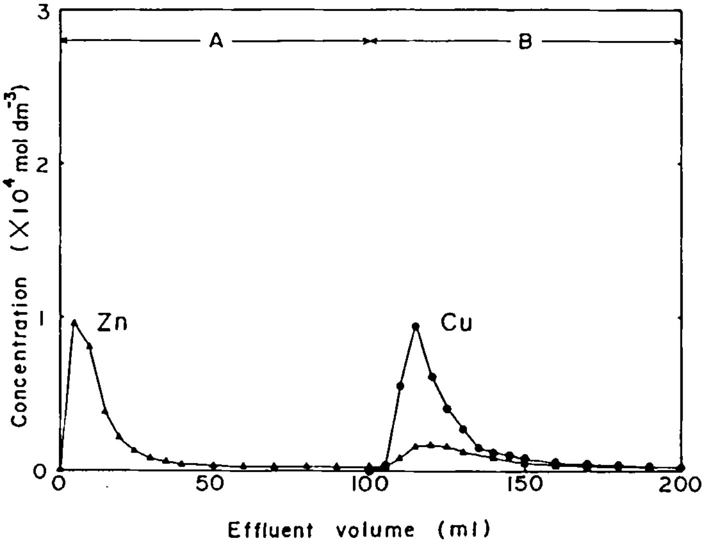

Fig. 3a. Mutual separation of copper ion from zinc ion. A: 0.001 *M* HNO_3. B: 0.5 *M* HNO_3.

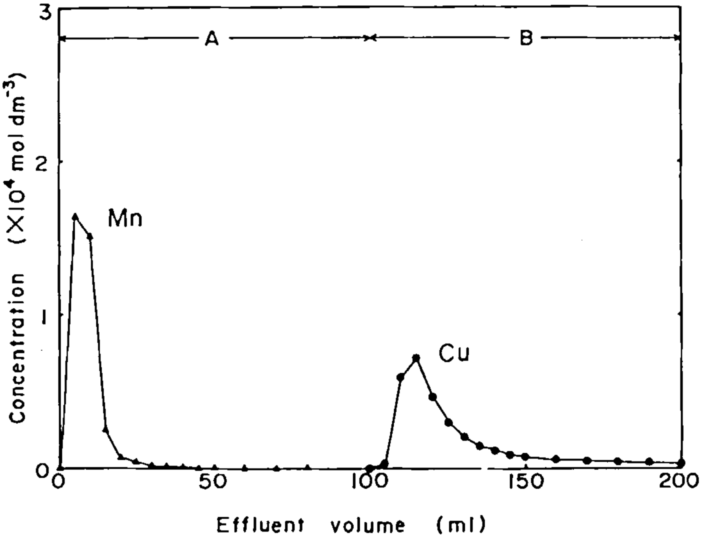

Fig. 3b. Mutual separation of copper ion from manganese ion. A: 0.001 *M* HNO_3. B: 0.5 *M* HNO_3.

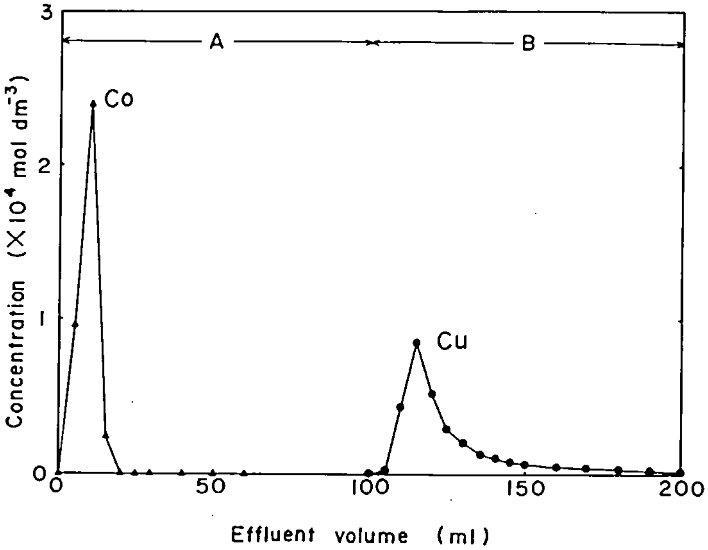

FIG. 3c. Mutual separation of copper ion from cobalt ion. A: 0.001 *M* HNO_3. B: 0.5 *M* HNO_3.

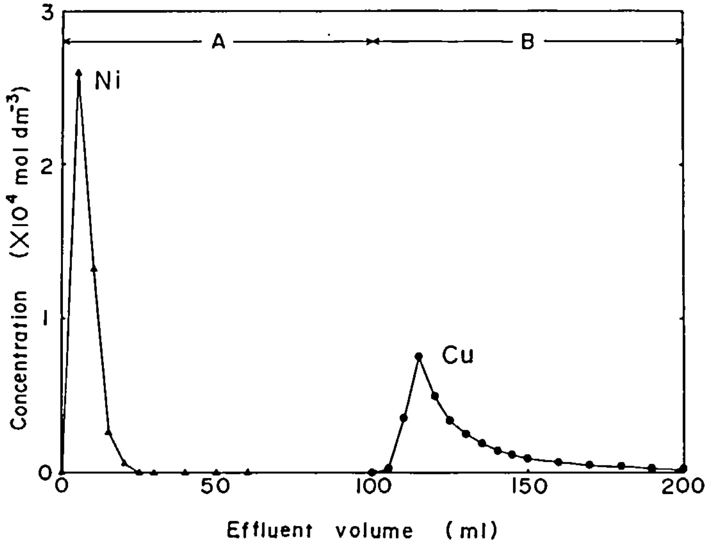

FIG. 3d. Mutual separation of copper ion from nickel ion. A: 0.001 *M* HNO_3. B: 0.5 *M* HNO_3.

These data show that this material is a good inorganic ion-exchanger which is useful for some separations.

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