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ABSTRACT

2-Ethylhexyl 2-ethylhexyl phosphonic acid was immobilized on a silica surface after treatment with dichlorodimethylsilane. Batch and fixed-bed tests were conducted in order to evaluate the metal ion removal capabilities using the prepared adsorbent (SDSP). Equilibrium isotherm data showed that the amount of adsorption is dependent on solution pH. The adsorption of zinc and the elution rate of the SDSP were examined, thus permitting a breakthrough curve to be obtained for the zinc solution. The adsorbed zinc ions were eluted with 0.1 M HCl. The elution ratio using a fixed bed was 91%. The selective recovery of zinc ion from Cu^{2+}, Cd^{2+}, and Co^{2+} was also investigated. The results showed that the SDSP adsorbed zinc ions selectively in the presence of Cu^{2+}, Cd^{2+}, and Co^{2+} in the 2–4 pH range. The effects of Mg^{2+}, Ca^{2+}, Na^+, Cl^-, NO_3^-, and SO_4^{2-} on the removal of zinc were relatively small.

INTRODUCTION

As a result of heavy metal ion release from industrial wastewater, water pollution has become a serious problem. Waste streams from industries contain solutions of metal ions, such as copper, nickel, zinc, cobalt, chromium (+6), lead, mercury, and aluminum (1).

Solvent extraction is widely used to remove metal ions from aqueous streams, but this extraction technology is known to be ineffective for aqueous metal concentrations below 0.01 mol/L (2). As an adsorption technology for

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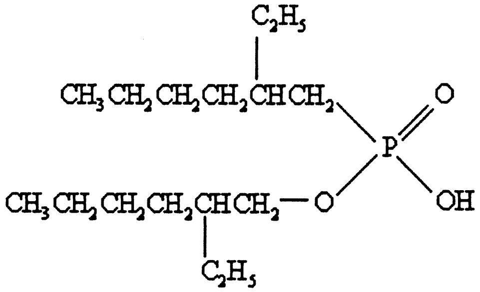

SCHEME 1 The structure of 2-ethylhexyl 2-ethylhexyl phosphonic acid (PC 88A).

removing heavy metals from dilute metal waste streams, silica supports impregnated with ion-chelating agents have been studied (3–11). This interest stems from its lack of swelling, good selectivity, rapid sorption of metal ions, and low loss of ion-chelating agents compared to solvent extraction, as well as its good mechanical stability (11). An adsorption process has some advantages over other methods because of its simplicity and sludge-free operation. Although the sorption capacities of such modified silica is relatively small, it can be efficiently used in the treatment of waste streams containing small quantities of heavy metal ions.

Ion-chelating organic molecules are usually chemically bonded to the silica surfaces through silanization procedures (3–10, 12). However, many ion-chelating agents may not contain a reactive functional group which is suitable for chemical bonding with a silanized inorganic surface. In this case, physical adsorption of organic chelating agents on the support offers an alternative possibility. Physical adsorption can be achieved through hydrophobic interactions, such as van der Waals forces (6, 13–15).

In a previous report, 2-ethylhexyl 2-ethylhexyl phosphonic acid (PC 88A) (see Scheme 1) was attached to a silica surface via silica surface silanization (16). The PC 88A would be expected to combine physically with the silanized silica surface via hydrophobic interaction. The adsorbent developed was found to be very stable at acidic conditions.

In this study the characteristics of the prepared adsorbent (SDSP) with respect to zinc ion adsorption are investigated. In addition, the selective removal of zinc ion from other divalent metal ions was examined.

EXPERIMENTAL

Materials and Apparatus

A powder-type silica (Aldrich Co.) was used as support. The characteristics of the supports are listed in Table 1. 2-Ethylhexyl 2-ethylhexyl phosphonic

TABLE 1
Properties of Silica Used as a Support[a]

Properties	
Surface area (m^2/g)	300
Diameter (mm)	0.149–0.074
Average pore diameter (nm)	15.0
Pore volume (mL/g)	1.15
Bulk density (g/mL)	0.34

[a] Data supplied by Aldrich Co.

acid (PC 88A, Daihachi Co.) was used as a chelating agent without further purification. Dichlorodimethysilane (Aldrich Chemical Co.) was used for chemical treatment of the silica support. $Zn(NO_3)_2 \cdot 6H_2O$ (Junsei Chemical Co.) was used to prepare solutions of zinc ions. Other metal ions (Ni^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+}) solutions were prepared from the metal nitrate salts which were of analytical grade (Junsei Chemical Co.). All other reagents were analytical grade. Buffer solutions were used to maintain the solution at a constant pH. 0.2 M KCl and 0.2 M HCl (pH 2), 0.1 M potassium hydrogen phthalate and 0.1 M HCl (pH 2.5, 3, 4), 0.1 M potassium hydrogen phthalate and 0.1 M NaOH (pH 5) were used to prepare the buffer solutions. The pH of the deionized water is about 5.5.

Metal ion concentrations were measured using an Atomic Absorption Spectrometer (Perkin-Elmer, Model 3110). A CHN Corder (Leco, Model CHNS-932) was used for elemental analysis to determine the amount of organic molecules in the substrates.

Preparation of Silica Immobilized with PC 88A

The silica immobilized with PC 88A was prepared as follows using silica which was initially dried at 100°C in an oven for 3 hours.

SDS: 10 g of dried silica was refluxed for 16 hours with 40 g of dichlorodimethylsilane. The silanized silica was then vacuum dried (30 mmHg) at 35°C to remove unreacted silane. The dried, derivatized silica was washed with deionized water to eliminate the remaining HCl and dried again at 30 mmHg, 45°C.

For impregnation with PC 88A, 40 g of a 30 wt% PC 88A in toluene was added to 10 g of silanized silica in a flask. The flask was shaken gently on a rotating shaker for 2 hours. The impregnated silica was then removed from the solution, initially dried at 50°C at atmospheric pressure, and then under vacuum (30 mmHg) at 50°C to completely evaporate toluene. The material (SDSP) was used in the experiments described below.

Adsorption and Elution

Equilibrium data were obtained by batch operations. The SDSP was placed in a flask containing 25 mL of metal ion solution. The flask was then placed on a shaker and rotated gently for 48 hours. Equilibrium isotherms were obtained by equilibrating 5 mmol/L zinc ion solutions with various quantities of the SDSP (0.15–2.0 g).

Leaching of the ligand by acidic solutions was experimentally measured. The SDSP was treated with buffer solutions at pH 2, 3, and 4 for 48 hours. After treatment, SDSP was filtered off and the organic contents in the remaining solutions were measured by an Inductively Coupled Plasma Spectrometer (Shimadzu ICPS-7500).

A transient adsorption experiment was carried out using a packed-column reactor. A Pyrex tube (inside diameter 11 mm) was packed with 1.0 g of the SDSP. The apparatus is also comprised of a circulation pump (Cole-Parmer) and a flow meter. 200 mL of feed solution containing zinc ion (2 mmol/L, pH 3) was fed to the reactor and recycled to the solution bath at a rate of 20 mL/min. After 70 minutes the adsorbed zinc ions were eluted successively using 100 mL of 0.1 M HCl solution.

To investigate the effect of repeated use on SDSP capacity, successive adsorption and elution rate data for SDSP were obtained using a packed-column reactor. SDSP (0.5 g) was treated with zinc solution (200 mL, 2 mmol/L, pH 4) and then 50 mL of 0.1 M HCl solution was fed to the reactor at a rate of 20 mL/min in order to desorb the zinc ions from the adsorbents. This operation was repeated for a total of six adsorption and elution cycles. Each operation time was 6 hours.

The breakthrough behavior of zinc ion was examined by passing a zinc solution (1 mmol/L) through a packed-column (ID 16 mm) loaded with 5 g of the adsorbent. The flow rate was maintained at about 5 mL/min. In this case the zinc solution was prepared from unbuffered deionized water. The pH of the zinc solution was 4.3. The elution experiment was conducted after the SDSP was nearly saturated with zinc ions. A 0.1 M HCl solution was fed to the reactor at a rate of 5 mL/min in order to elute the zinc ions from the SDSP.

The selectivity of the SDSP for zinc ion from Cu^{2+}, Cd^{2+}, and Co^{2+} were also investigated. Competitive adsorption experiments were carried out using metal aqueous solutions of metal ions containing Zn^{2+} and either Cu^{2+}, Cd^{2+}, or Co^{2+}. In these experiments, 0.2 g of SDSP was added to 25 mL of a binary aqueous solution at a concentration of 5 mmol/L and equilibrated for 24 hours. The solution pH range was 2 to 5.

Selective removal of the SDSP for zinc ions from copper ions was examined using a packed column (ID 16 mm). A mixed solution of zinc and copper (1 mmol/L) was passed through the packed column loaded with 5 g of the adsorbent. Breakthrough curves for zinc and copper ion were then obtained. The flow rate was about 5 mL/min. In this case the solution was prepared from unbuffered, deionized water. The pH of the feed solution was adjusted to around 4.0 by HCl solution.

The effect of salts such as NaCl, $NaNO_3$, and Na_2SO_4 on the adsorption capacity of zinc ion was also investigated. 5 mmol/L zinc solutions (pH 4) containing various quantities (0.01–1.0 mol/L) of NaCl, $NaNO_3$, and Na_2SO_4 were equilibrated with 0.1 g of the SDSP, and the amount of adsorbed zinc was then determined. The effect of the presence of Ca^{2+} and Mg^{2+} on the zinc adsorption capacity was also examined. The SDSP was equilibrated with a solution containing Zn^{2+} and Ca^{2+}, and a solution containing Zn^{2+} and Mg^{2+}. The zinc ion concentration of the two solutions was 5 mmol/L, and the concentrations of the alkaline earth metal ions were varied (0.01–1.0 mol/L).

RESULTS AND DISCUSSION

Immobilization of PC 88A

The surfaces of the silica prepared after silanization are functionalized as follows (6, 16):

$$\text{SDS:} \quad 2(\equiv\text{Si—OH}) + \text{Cl}_2\text{Si(CH}_3)_2 \rightarrow (\equiv\text{Si—O})_2\text{Si(CH}_3)_2 + 2\text{HCl} \quad (1)$$

Since the methyl groups on the silanized silica would not be expected to form chemical bonds with the PC 88A molecules, it is likely that the PC 88A would bind with hydrocarbon chains on the silanized surface by noncovalent bonding such as van der Waals interactions. In this case the binding force is probably considerably weaker than that of chemical adsorption.

Results of the leaching experiment showed that approximately 5–7% of immobilized PC 88A molecules were leached by acidic solution of pH 2, 3, and 4. SDSP showed good stabilities under acidic conditions although surface–hydrophobic interactions are expected.

Equilibrium Isotherm

The reaction scheme for PC 88A with trace levels of a divalent metal ion M^{2+} is generally thought to occur as follows (17–21):

$$m\text{M}^{2+} + m(n+1)\overline{(\text{HR})_2} \rightleftharpoons \overline{(\text{MR}_2 n(\text{HR})_2)_m} + 2m\text{H}^+ \quad (2)$$

Here, $\overline{\text{HR}}$ and $\overline{(\text{HR})_2}$ represent the monomeric and dimeric species of the PC 88A, respectively. $\overline{(\text{MR}_2 n(\text{HR})_2)_m}$ is the polymeric form of the metal–PC 88A complex. From Eq. (2), the equilibrium constant can be expressed as

$$K_1 = \frac{[\overline{(\text{MR}_2 n(\text{HR})_2)_m}][\text{H}^+]^{2m}}{[\text{M}^{2+}]^m[\overline{(\text{HR})_2}]^{m(n+1)}} \quad (3)$$

On the other hand, at conditions of high metal loading, the reaction in the organic phase may occur as follows (17):

$$M^{2+} + 2\overline{HR} \rightleftharpoons \overline{MR_2} + 2H^+ \tag{4}$$

In this case the equilibrium constant can be defined as follows:

$$K_2 = \frac{[MR_2][H^+]^2}{[M^{2+}][HR]^2} \tag{5}$$

Figure 1 shows the equilibrium isotherm of the SDSP which is in contact with the aqueous solution of zinc ions at solution pH values of 2.5, 3, and 4. The results show that the amount of zinc ions extracted from the aqueous solution increases with the pH of the solution. The adsorption capacity for zinc of the SDSP at pH 2 was very small. A capacity of 0.03 mmol/g was obtained in the 0.35–0.45 mmol/L solution concentration range. The extraction capacity of the SDSP increases considerably when the solution pH is shifted from 2.0 to 2.5. The increase is also abrupt in the range of pH 2.5 to 3, as shown in Fig. 2. The extraction efficiency increases considerably for a pH change from 3 to 4 in the low concentration range (below about 1.0 mmol/L). However, at high concentration ranges (above about 1.0 mmol/L), the adsorption capacities for pH 3 and 4 show nearly the same value, remaining constant with increasing solution concentration. For pH 4, the SDSP was nearly saturated above a solution concentration of about 0.3 mmol/L.

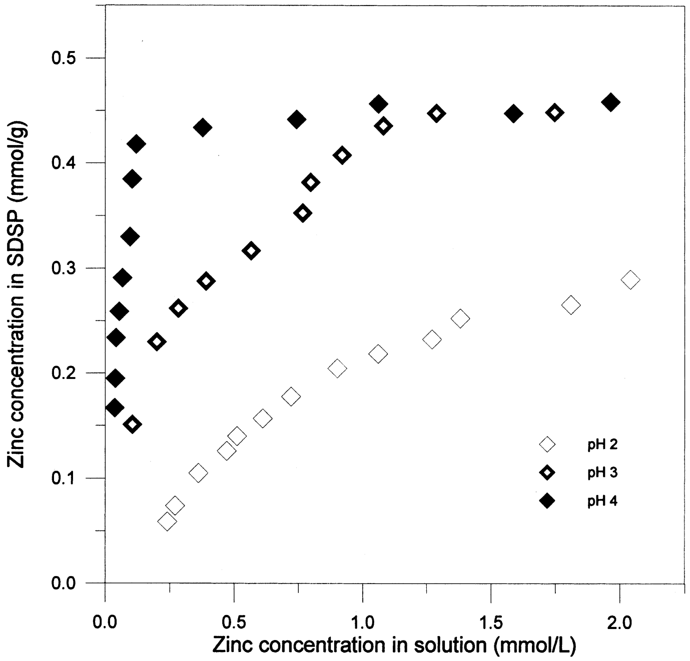

FIG. 1 Equilibrium isotherms of the SDSP at various solution pHs.

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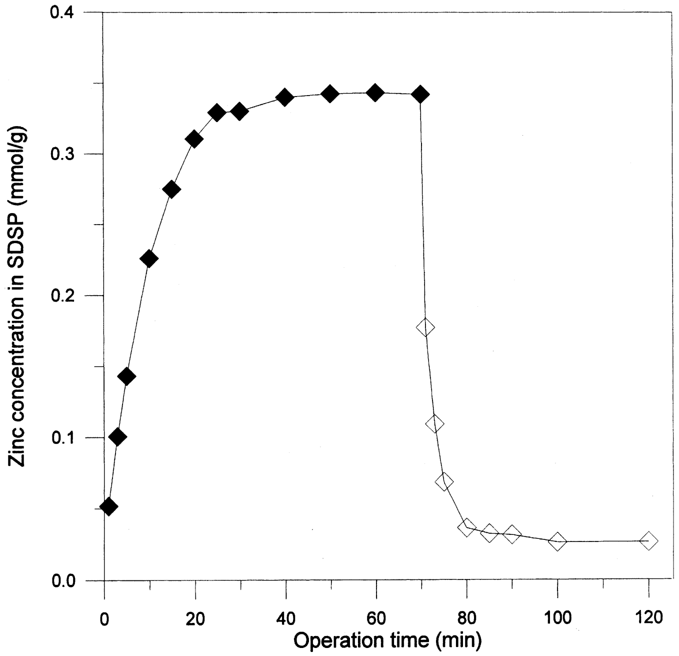

FIG. 2 Transient zinc concentration changes for packed-column operation using the SDSP. Solution: 2 mmol/L, 200 mL, pH 3. SDSP: 1 g.

The experimental results were compared with the calculated values using Eq. (5) for the various solution pHs in order to check the validity of Eq. (5). An optimization program (UNLSF in IMSL) was used to determine the value of the equilibrium constant K_2 to minimize differences in experimental data and calculated value at the three pHs. However, significant errors were introduced using the determined K_2 value. This result indicates that Eq. (5) might not be valid for expressing the reaction mechanism between PC 88A and zinc ion at low metal loading. In this experiment the net concentration of PC 88A in the SDSP was about 1.06 mmol/g as evidenced by carbon analysis. When it is assumed that the PC 88A in the SDSP reacts with zinc ion as described by Eq. (4) at high metal loading, the theoretical zinc adsorption capacity is 0.503 mmol/g. The maximum zinc adsorption capacity is approximately 0.46 mmol/g as shown in Fig. 1. This value represents 88% of the theoretical maximum capacity. These results indicate that either the pores of the SDSP were partially blocked by the organic compounds, and that the PC 88A molecules did not react completely with zinc ions, or the adsorption reaction by Eq. (2) occurred.

Kinetic Performance

The kinetic performances of the SDSP for treating a zinc solution are shown in Fig. 2. 1.0 g of the SDSP was used for 200 mL of a 2 mmol/L zinc ion solution. Experiments were carried out using a packed-column reactor. The rate

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of relative concentration in solution decreased rapidly for about 20 minutes and then decreased more slowly. Apparent equilibrium was reached after about 60 minutes. The elution of adsorbed zinc ion was carried out using 100 mL of a 0.1 M HCl solution. The stability of the SDSP for 0.1 M HCl solution was found to be very high in our previous work (20). The elution of zinc ion was faster than that of adsorption as shown in Fig. 2. 47% of the adsorbed zinc ions were eluted within 1 minute. Apparent equilibrium was reached after 20 minutes for the elution process. About 90% of the adsorbed zinc ions were eluted after 20 minutes, and a concentration factor of 1.6 was obtained.

Breakthrough Curve for Zinc Ion

A breakthrough experiment was carried out for the SDSP using a packed-column reactor (ϕ 16 mm). The result of the breakthrough behavior experiment (Fig. 3) showed that about 140 bed volumes of feed solution could be passed through the adsorbent with below 1 ppm of zinc ion in the effluent. The zinc concentration in the effluent was increased up to the saturation point after about 380 bed volumes. At 483 bed volumes, a capacity of 0.456 mmol/g was achieved.

The elution of zinc ions from the sample after using the breakthrough curve experiment was then studied. A solution of 0.1 M HCl was passed through the bed at a rate of 5 mL/min. As shown in Fig. 4, the zinc concentration of the

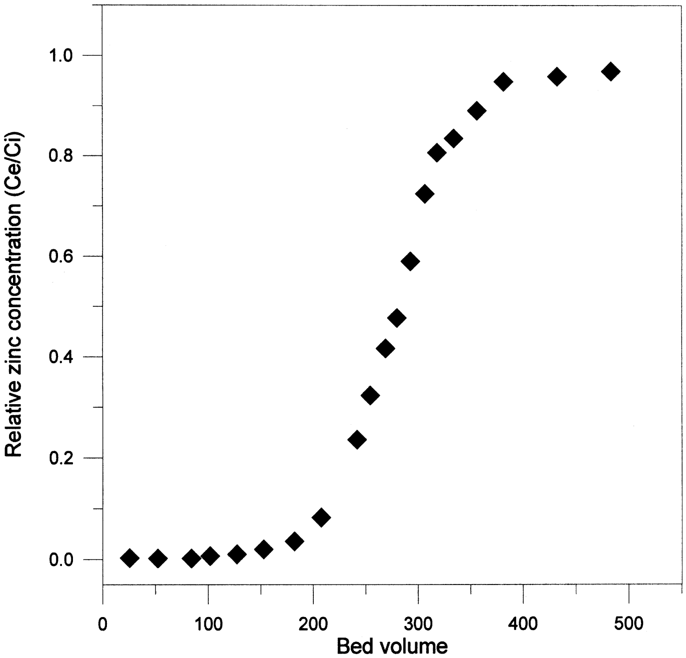

FIG. 3 Breakthrough curve for zinc ions using the SDSP. Feed solution: 1 mmol/L, pH 4.3, 5 mL/min. SDSP: 20 g. Bed diameter: 16 mm.

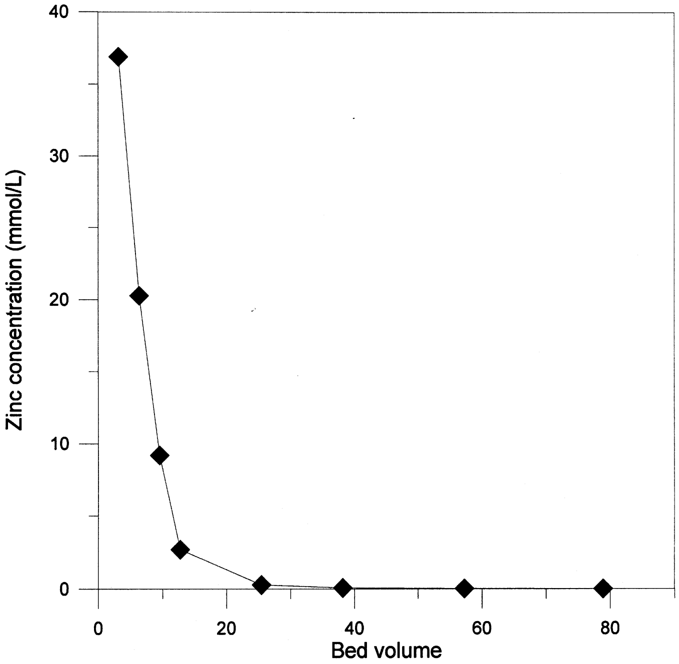

FIG. 4 Elution of zinc ions using the SDSP. Elution solution: 0.1 M HCl, 5 mL/min. SDSP: 5 g, initial zinc loading 0.456 mmol/g. Bed diameter: 16 mm.

effluent was initially very high and then decreased dramatically within about 20 bed volumes. This result indicates that the rate of elution is faster than that of adsorption; 91% of the zinc ions were eluted in up to 89 bed volumes. The average concentration of the initial 89 bed volumes was 3.35 mmol/L. Since the inlet concentration was 1 mmol/L, a concentration factor of 3.35 was obtained for the initial 89 bed volumes.

Separation of Zinc Ion from Binary Solution

The extractabilities of the SDSP for various heavy metals were examined. Figures 5–7 depict the percentage extraction of metal ions in a single solution and those in binary solutions containing Zn^{2+} and either Cu^{2+}, Co^{2+}, or Cd^{2+} as a function of solution pH. The order of metal ion capacity values of the four tested metal ions is $Zn^{2+} > Cu^{2+} \cong Cd^{2+} > Co^{2+}$. The extraction capability for zinc ion increased dramatically with pH from a solution pH of 2.0 to 3.0, and increased slightly for values above pH 3 for all cases. This zinc ion removal capacity was reduced slightly by the presence of other metal ions, as shown in the figures. However, the adsorption of other metal ions was seriously interfered with by the presence of zinc ions. The extractions of copper and cadmium were observed above pH 3 in single solutions. The extraction percentages of copper and cadmium ion were 51 and 49%, respectively, at pH

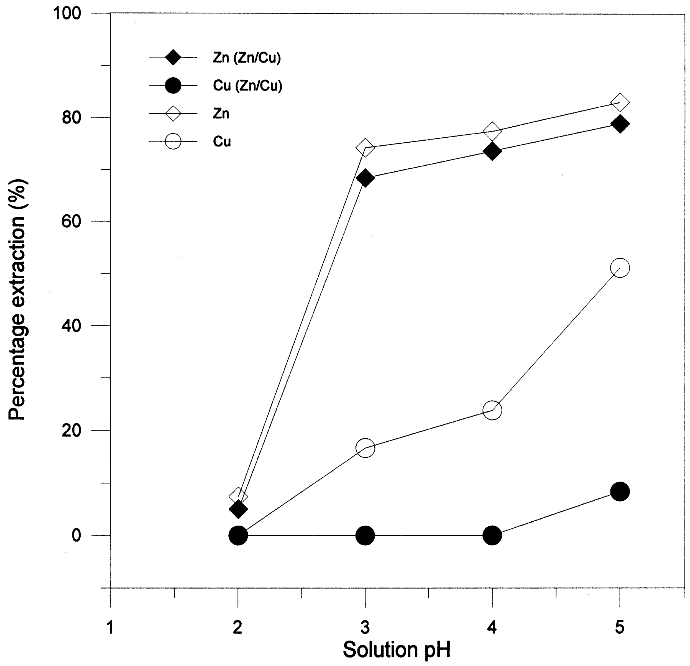

FIG. 5 Percentage extraction of Zn and Cu ions as a function of pH using the SDSP. Solution: 5 mmol/L, 25 mL. SDSP: 0.2 g.

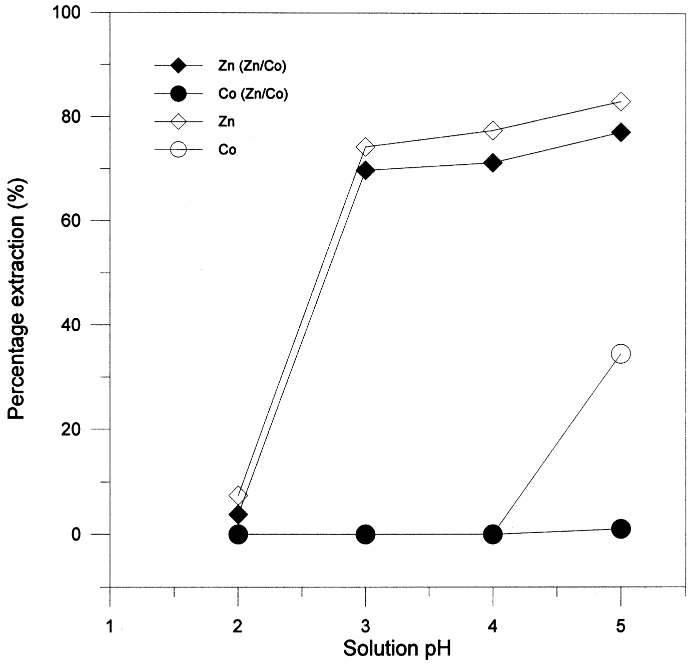

FIG. 6 Percentage extraction of Zn and Co ions as a function of pH using the SDSP. Solution: 5 mmol/L, 25 mL. SDSP: 0.2 g.

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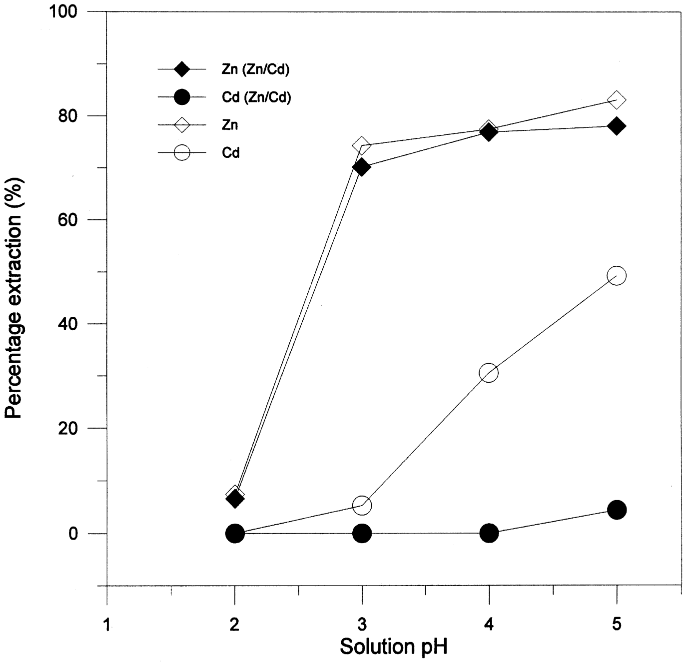

FIG. 7 Percentage extraction of Zn and Cd ions as a function of pH using the SDSP. Solution: 5 mmol/L, 25 mL. SDSP: 0.2 g.

3. However, in the case of a binary solution, copper and cadmium ions were extracted slightly at pH 5 (copper, 8.4%; cadmium, 4.4%). The removal of cobalt ions was reduced from 35 to 1.0% at pH 5 by the presence of zinc ions. The reduced capacity of metal ion extraction can be explained by the competitive adsorption of zinc ion and another metal ion. The results of the selectivity experiments show that the selective removal of zinc ion from solutions of Cu^{2+}, Cd^{2+}, and Co^{2+} is possible below pH 4. Selective removal of zinc ion from nickel ion would also be possible, since the capacity of PC 88A for nickel ion below pH 4 is reported to be negligible (17). The quantitative removal of Cu^{2+}, Cd^{2+}, and Co^{2+} by the SDSP would be possible about pH 5 after previous removal of zinc ions by the SDSP. The pH dependence and the selectivities of the SDSP are in good agreement with the work of Owusu in the similar system (22).

Separation of Zinc Ion from Copper by a Fixed-Bed Reactor

The zinc selectivity of the SDSP over copper was investigated using a fixed-bed reactor. Figure 8 shows the breakthrough curves for a binary solution containing Zn^{2+} and Cu^{2+}. The concentration of each metal was 1 mmol/L, and the inlet solution pH was controlled at pH 4. Approximately 150

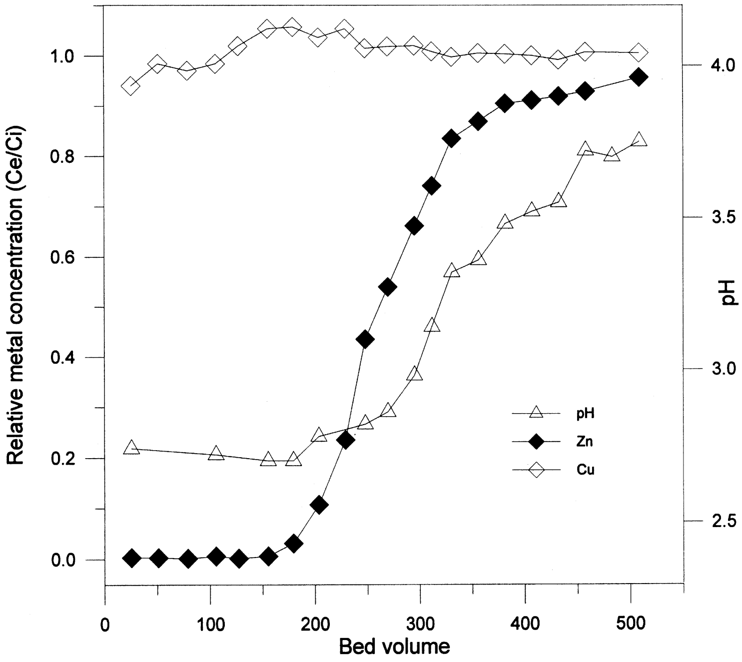

FIG. 8 Breakthrough curves for copper ions for a binary solution containing Zn^{2+} and Cu^{2+} using the SDSP. Feed solution: 1 mmol/L, pH 4, 5 mL/min. SDSP: 5 g. Bed diameter: 16 mm.

bed volumes of feed solution can be passed through while maintaining the zinc concentration below 1.0 ppm in the effluent. The zinc concentration in the effluent increased and the adsorbent became saturated after about 510 bed volumes. A capacity of 0.455 mmol/g was achieved. This value is nearly equal to that for the case of extraction of the zinc alone. On the contrary, copper ion was not adsorbed, as shown in the figure. The effluent pH increased from 2.7 at 25 bed volumes to 3.8 at 510 bed volumes. The change of pH coincides with that of the effluent zinc concentration. The effluent zinc concentration and the pH increased rapidly and simultaneously from approximately 200 bed volumes to 350 bed volumes. These results indicate that the SDSP selectively adsorbs zinc ion in the presence of copper ion under the conditions employed here. The selective and quantitative removal of zinc ion from Cd^{2+}, Co^{2+}, and Ni^{2+} using a fixed-bed reactor would also be possible if the inlet solution pH were controlled at approximately 4.

Effect of Salts

Anions such as Cl^-, NO_3^-, and SO_4^{2-} are capable of affecting the removal of metal ions by PC 88A. Chloride ion has the ability to form complexes with many metal ions. The effects of NaCl, $NaNO_3$, and Na_2SO_4 on the adsorption

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capacity of zinc ion were investigated for 5 mmol/L zinc solutions. The pH of the solutions was maintained at a constant value using a pH 4 buffer solution. The concentration range of the salts was 0.01–1.0 mol/L. Figure 9 shows the change of zinc adsorption capacities of the SDSP with the concentration of the salts. Here, the relative extraction is defined as the ratio of the amount of zinc adsorbed to that for the single zinc solution. The extraction data are scattered and disorderly, reaching both a maximum and a minimum. However, it may be concluded from the results that the presence of Cl^-, NO_3^-, and SO_4^{-2} as well as Na^+ has a relatively small effect on zinc adsorption capacity. The zinc removal capacity was reduced by less than 10% by the salts in the 0.01–1.0 mol/L concentration range.

Industrial wastewater or natural water often contains Ca^{2+} and Mg^{2+}. Hence, the effect of Ca^{2+} and Mg^{2+} on zinc adsorption was investigated. The concentration of $Ca(NO_3)_2$ and $Mg(NO_3)_2$ were varied from 0.01 to 1.0 mol/L. The results of the experiments are illustrated in Fig. 10. The relative extraction ratios were between 88 and 99% for Ca^{2+} and between 89 and 99% for Mg^{2+} within a 0.01–1.0 mol/L concentration range. The amount of zinc removal reaches a maximum at a salt concentration of 0.4 M for both salts. The results show that the effects of Ca^{2+} and Mg^2 are relatively small on the adsorption of zinc by the SPDP.

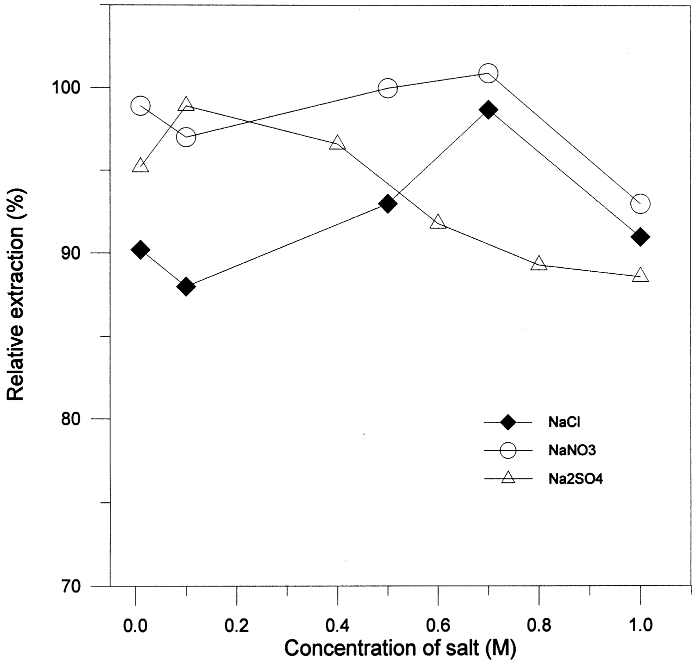

FIG. 9 Relative extraction of zinc ion as a function of NaCl, $NaNO_3$, and $Na_2(SO_4)_2$ concentration.

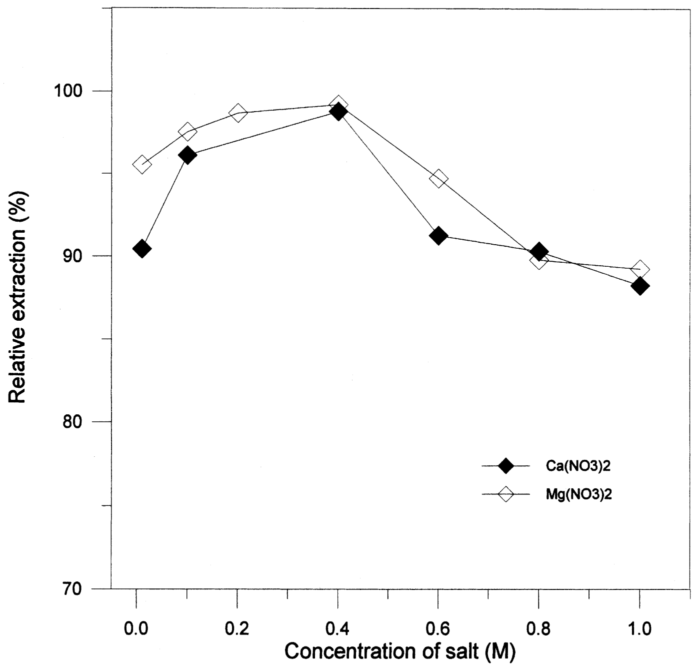

FIG. 10 Relative extraction of zinc ion as a function of $Ca(NO_3)_2$) and $Mg(NO_3)_2$ concentration.

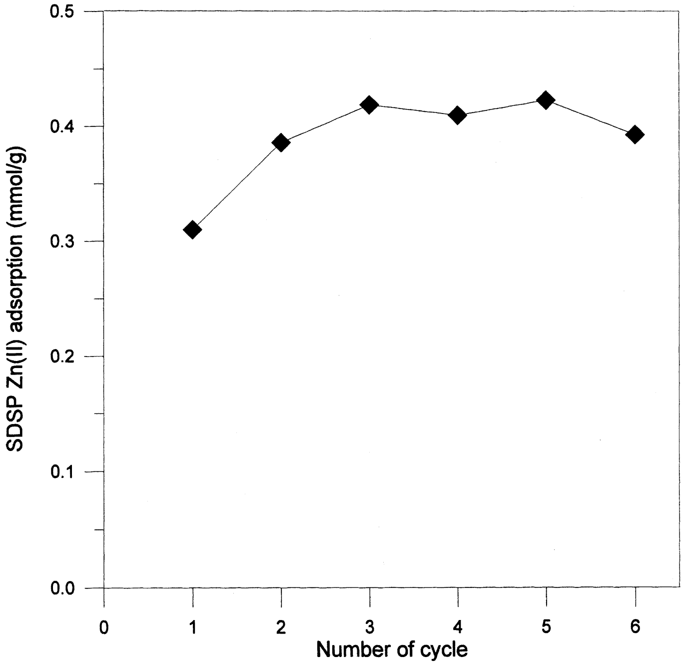

FIG. 11 Successive adsorption–elution of the SDSP: SDSP 0.5 g, zinc solution 2 mmol/L; 200 mL; pH 4, elution solution 0.1 M HCl; 100 mL; adsorption and desorption operation time 6 hours.

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Successive Adsorption and Elution

Successive adsorption and elution results provide data on the effect of repeated use of SDSP samples on adsorption capacity. Figure 11 shows the change of zinc adsorption capacity during successive operations. The adsorption capacity increased from 0.31 mmol/g for the first operation to 0.42 mmol/g for the third operation and then decreased to 0.39 mmol/g for the sixth operation. The initial low adsorption capacity may be explained by the low adsorption rate due to surface hydrophobicity. The decrease in adsorption capacity after the third operation is probably due to incomplete elution and loss of PC 88A. The elution ratios were approximately 95–100% by contact with acidic solutions. These results indicate that SDSP is feasible for cyclic use after regeneration with acidic solutions.

CONCLUSION

PC 88A was immobilized on the surface of the silica supports after surface silanization. The results of equilibrium isotherm experiments showed that the adsorption capacity for zinc ions is a function of solution pH and solution metal concentration. Breakthrough and elution studies show that the SDSP can be used effectively for the removal of zinc ions using a once-through fixed-bed operation. Adsorbed zinc ions can be recovered by treatment with an acidic solution, and the concentration of the zinc solution was obtained. The selective and quantitative removal of zinc ions from Cu^{2+}, Cd^{2+}, and Co^{2+} was possible in the 3–4 pH range. The quantitative removal of Cu^{2+}, Cd^{2+}, and Co^{2+} by the SDSP would also be possible above about pH 5 after the zinc ions had been removed previously by SDSP. The influence of Mg^{2+} and Ca^{2+} on zinc removal was relatively small, as well as was that of Cl^-, NO_3^-, and SO_4^{2-}.

SYMBOLS

C_e	zinc ion concentration in the effluent (mol/L)
C_i	zinc ion concentration in the feed (mol/L)
$\overline{HR}$	monomeric species of the PC 88A
$\overline{(HR)_2}$	dimeric species of the PC 88A
K_1	equilibrium constant of the reaction described by Eq. (3) $(g/mol)^{1-m(n+1)}(mol/L)^m$
K_2	equilibrium constant of the reaction described by Eq. (6) (g/L)
M	metal
$\overline{MR_2(HR)_n}$	metal-PC 88A complex in Eq. (2)
MR_2^-	metal-PC 88A complex in Eq. (5)
[ ]	concentration (mol/L for solution phase, mol/g for solid phase)
overline	solid phase

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