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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
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Online publication date: 23 April 2002

To cite this Article Tanaka, David A. Pacheco , Kerketta, Sunamani , Tanco, Margot A. Llosa , Yokoyama, Toshiro and Suzuki, Toshishige M.(2002) 'Adsorption of fluoride ion on the zirconium(IV) complexes of the chelating resins functionalized with amine-*N*-acetate ligands', Separation Science and Technology, 37: 4, 877 — 894

To link to this Article: DOI: 10.1081/SS-120002221

URL: http://dx.doi.org/10.1081/SS-120002221

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SEPARATION SCIENCE AND TECHNOLOGY, 37(4), 877–894 (2002)

ADSORPTION OF FLUORIDE ION ON THE ZIRCONIUM(IV) COMPLEXES OF THE CHELATING RESINS FUNCTIONALIZED WITH AMINE-*N*-ACETATE LIGANDS

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ABSTRACT

The reaction of fluoride ion with Zr(IV)-ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (EDTA) complexes has been examined by ^{19}F and ^{1}H NMR spectroscopies and potentiometry using [Zr(H_2O)$_2$EDTA] and K_2[Zr(CO_3)EDTA] as the model compounds. Ternary complex formation has been suggested as the most plausible mechanism for the retention of fluoride ion on the Zr(IV) complexes. Removal of fluoride ion has been attempted by the use of polymer homologues of Zr(IV)–EDTA complexes. Adsorption characteristics of fluoride ion on Zr(IV) complexes of the chelating resins [CMA (carboxymethylamine) and IDA (iminodiacetic acid) resins] have been investigated. The adsorption capacities and the binding constants for fluoride ion on the Zr(IV) loaded resins have been analyzed using Langmuir

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model of adsorption. Common anions including chloride, nitrate, acetate, and sulfate ions did not interfere significantly with the adsorption of fluoride ion, whereas the presence of phosphate ion reduced the fluoride capacity markedly. The adsorption rate of fluoride ion uptake by Zr-CMA resin is much faster than that of the Zr-IDA resin. A column process including adsorption, desorption, and regeneration cycles has been demonstrated for the removal of fluoride ion to depict a practical application.

Key Words: Separation; Fluoride ion; Zr(IV)–EDTA complex; Polymer chelating resin

INTRODUCTION

In recent years, appreciable amounts of hydrofluoric acid and ammonium fluoride have been used in the electronics and semiconductor industries as washing and etching reagents (1). Similarly, fluorides are being used in fertilizer, aluminum industries, and water additives. Underground water also often contains high level of fluoride ion, which has caused serious illnesses like skeletal and dental fluorosis in some countries (2,3). Therefore, removal of fluoride ion from industrial effluents or drinking water systems has become increasingly important. Due to its high electronegativity and small ionic size, fluoride ion is classified as a hard base, which has strong affinity towards multivalent metal ions including Al(III), Ca(II), Fe(III), Zr(IV), and a series of lanthanide metal ions (4). Generally, fluoride ion is treated by coagulation and precipitation processes by the formation of calcium or aluminum fluoride (5,6). However, trace amounts of fluoride ion tend to remain in the solution due to the solubility restriction of the salts. In addition, a large amount of wet bulky sludge is inevitably generated. On the other hand, a column process with solid adsorbent provides a number of advantages in separation and concentration of trace amounts of ions from a large quantity of water due to the high enrichment efficiency, ease in phase separation and generally, does not require special chemicals.

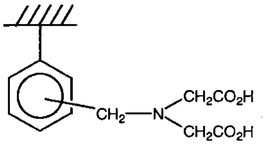
Inorganic anion exchangers including hydrous metal oxides (M = Al, La, Ce, Zr) (7–12) and metal ion loaded amine, aminocarboxylate, and aminophosphonate chelating resins (13–15) have been studied and patented as the materials applicable to selective removal of fluoride ion. Retention of fluoride ion on hydrous metal oxides has been interpreted by the ion exchange mechanism based on the electrostatic attraction force (10,12). Yuchi et al. suggested that adsorption of fluoride ion on Zr(IV) complexes takes place by dual mechanisms: an ion-exchange mechanism in strongly acidic media and the addition reaction in weakly acidic media (16). Recently, we have demonstrated that several types of oxo-anions are bound to Zr(IV) center of Zr(IV)-ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (EDTA) directly by ternary complex formation (17).

In the present work, we have studied the reaction mechanism between fluoride ion and Zr(IV) complexes by ^{19}F NMR and potentiometry using $K_2[Zr(CO_3)EDTA]$ and $[Zr(H_2O)_2EDTA]$ as the model compounds. Furthermore, we have prepared Zr(IV) complexes of polymer chelating resins having amine-*N*-acetate group as depicted in Fig. 1. Since Zr(IV)–EDTA complex is extremely stable, we attempted to fabricate the Zr(IV) complex of polymer resin having the functional group of EDTA analogue. The CMA resin is expected to form a stable 1:1 complex with Zr(IV), since the functional group formally has two sets of iminodiacetate group. Similarly, the Zr(IV) complex of conventional chelating resin having iminodiacetate [IDA (iminodiacetic acid) resin] was prepared for comparison. Adsorption properties of these resins for the fluoride ion have been investigated with respect to percent extraction, effect of diverse ions, kinetics, and column adsorption.

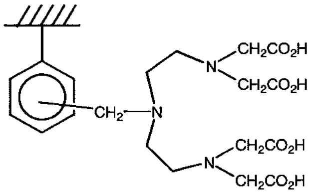
EXPERIMENTAL

Chemicals

Stock solutions of zirconium and fluoride ions were prepared by dissolving analytical grade of $ZrOCl_2 \cdot 8H_2O$ and sodium fluoride, respectively.



IDA-resin



CMA-resin

Figure 1. Schematic drawings of the IDA-resin and the CMA-resin.

$K_2[Zr(CO_3)EDTA]\cdot 3H_2O$ was prepared by mixing the aqueous solutions of $ZrOCl_2\cdot 8H_2O$ and EDTA followed by adjusting the pH to 5.5 with K_2CO_3. The molecular structure of the complex was confirmed by x-ray crystallography in our previous work (17). We obtained the crystals of $[Zr(H_2O)_2EDTA]$ by hydrolysis of the carbonato complex with hydrochloric acid.

Preparation of the Zr(IV) Loaded Resins

The polymer matrix of the IDA resin and the CMA resin is macroporous type styrene–10%-divinylbenzene copolymer (30–60 mesh) with a surface area and mean pore diameter of $7.3\,m^2\,g^{-1}$ and 720 Å, respectively. The CMA resin used in the present study was prepared as reported previously (18). Thus, N-carboxymethylation of the diethylenetriamine-bound polystyrene resin with sodium bromoacetate gave the CMA resin. The IDA resin was prepared according to the procedure described before (19) starting from the same polymer matrix as with the CMA resin. The physical properties of these chelating resins are listed in Table 1. Zirconium(IV) was loaded onto the CMA resin by stirring the resin (40 g) with aqueous solution of $ZrOCl_2\cdot 8H_2O$ (80 g in $200\,cm^3$ of 1 *M* HCl) overnight. The Zr(IV) chelated resin beads (Zr-CMA) thus obtained were washed thoroughly with water and ethanol and then dried under reduced pressure at 50°C. The zirconium content in the resin was determined by degradation of the resin by heating with 70% perchloric acid followed by inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis. The zirconium content in the Zr-CMA resin was $0.82\,mmol\,g^{-1}$. Loading of Zr(IV) onto the IDA resin was carried out in a manner similar to that for the Zr-CMA resin and the zirconium content was found to be $0.54\,mmol\,g^{-1}$.

Table 1. Physical Data of the Chelating Resins

	IDA Resin	CMA Resin
Polymer matrix	MR-styrene–DVB[a]	MR-styrene–DVB[a]
Particle size	30–60 mesh	30–60 mesh
Mean pore diameter (Å)	720	720
Surface area ($m^2\,g^{-1}$)	7.3	7.3
Ligand content ($mmol\,g^{-1}$)	3.0	1.65
Zr(IV) content ($mmol\,g^{-1}$)	0.54	0.82
Bead density ($g\,cm^{-3}$)	0.52	0.45

[a] MR-styrene–DVB = Macroreticular styrene–divinylbenzene copolymer.

Measurements

The concentration of fluoride ion was measured by fluoride ion selective electrode equipped on the ion meter, DKK Model IOL-40 (DKK Co.) in conjunction with a reference electrode. The fluoride ion concentration was calculated by the calibration curve prepared with the standard solutions. Potentiometric titration was performed using a TOA AUT 501 (TOA Electronics Ltd.) auto-titrator equipped with an auto-burette and a water-jacketed titration vessel. Zirconium concentration was determined by an inductively coupled plasma atomic emission spectrometer SEIKO Model SPS-1200A (SEIKO Instruments Inc.). The ^{1}H- and ^{19}F NMR spectra were measured at room temperature in D_2O with a Varian INOVA-500 spectrophotometer. The ^{19}F chemical shifts were expressed relative to the signal of fluoride ion (NaF). A digital pH meter, TOA HM-265 (TOA Electronics Ltd.) was used for pH measurements. The pH values of the solutions were adjusted with acetate buffer in the pH ranging 4–7 and with ammonia/ammonium chloride buffer in the pH 7–10 region. The pH values of the solutions less than 4 were adjusted with HCl solution and pH values more than 10 were adjusted with NaOH solution.

Determination of Ternary Complex Formation Constant

Equilibrium constants of the ternary complex formation with fluoride ion were determined by potentiometric titration using fluoride ion selective electrode. The titration vessel was filled with $100\,\mathrm{cm}^3$ of $3.5 \times 10^{-4}\,M$ fluoride ion solution of pH 5.0 and then fluoride selective electrode was immersed. To this solution was added $5.9 \times 10^{-3}\,M$ of $[\mathrm{Zr(H_2O)_2EDTA}]$ dropwise using an auto-burette. Potential reading was recorded at appropriate intervals to obtain potential vs. titration volume relation. The reaction of ternary complex formation was assumed to proceed by the following scheme:

$$[\mathrm{Zr(H_2O)_2EDTA}] + \mathrm{F}^- = [\mathrm{ZrF(H_2O)EDTA}]^- + \mathrm{H_2O} \qquad (1)$$

$$[\mathrm{ZrF(H_2O)EDTA}]^- + \mathrm{F}^- = [\mathrm{ZrF_2EDTA}]^{2-} + \mathrm{H_2O} \qquad (2)$$

The equilibrium constants of the above reactions were determined by fitting the calculated and observed potential data, i.e., refine the parameter to minimize the square of the difference between the observed and calculated potentials at each titration point (20). The calculated potentials were obtained using mass balance equations and the concentrations of fluoride ion and total $[\mathrm{Zr(H_2O)_2EDTA}]$.

Percent Extraction of Fluoride Ion

The percent extraction of fluoride ion by the Zr-IDA or Zr-CMA resin was obtained as follows, where the amount of fluoride ion is always smaller than the zirconium content of the respective resins. A 0.5 g portion of Zr-IDA or Zr-CMA resin was added to the solution containing 5 cm^3 of 0.02 *M* fluoride ion solution, 30 cm^3 of water and then the pH was adjusted with a buffer solution. The suspension was shaken for 6 days at 25°C, and then the equilibrium pH was measured. Resin beads were filtered off and the solution was diluted to 50 cm^3. The amount of fluoride ion remaining in the solution was determined, and the percent extraction was calculated by the difference in fluoride concentrations between the initial and the equilibrated solutions.

Adsorption Isotherm

Typically, 0.5 g portion of Zr-IDA or Zr-CMA resin was added to various concentrations of fluoride ion solution, at pH 5. The total volume of the solution was adjusted to 35 cm^3 by the addition of water. Then the suspension was shaken for 6 days at 25°C. After the equilibrated pH was measured, resin beads were filtered off and diluted to 50 cm^3. The amount of fluoride ion present in the equilibrated solution was determined. The capacity of the resins (C_s) and equilibrium constant (K) were calculated by using the Langmuir isotherm equation (21,22).

Kinetic Study

The time course of fluoride uptake by the Zr-loaded chelating resins was carried out at pH 5.0 typically by the following procedure. Four grams of Zr-CMA resin was stirred with buffered fluoride ion solution (5.8 *mM*, 300 cm^3) at constant rotation of 400 rpm. The reaction temperature was maintained at 25°C by immersing the vessel in a thermostated water bath. The concentration of fluoride ion was measured directly by the ion-meter at an appropriate interval. The kinetic data was analyzed by Vermeulen's approximation (23,24).

Column Adsorption Experiments

The column adsorption of fluoride ion was carried out by a column packed with 4 g of the Zr-CMA (8.9 cm^3) or Zr-IDA (7.7 cm^3) resin. The resin was soaked in water overnight prior to column packing. After packing into column, the resin was conditioned with a buffer solution of pH 5. A feed solution containing 10 ppm of fluoride ion adjusted at pH 5 with acetate buffer was passed continuously through the column at various feed rates. The effluent solution from the column was fractionated into 19.0 cm^3 portions and the concentration of fluoride ion was analyzed. In a similar manner fluoride ion (10 ppm) dissolved in seawater was treated with the CMA resin column at pH 4.

RESULTS AND DISCUSSION

Ternary Complex Formation of Zr-EDTA with Fluoride Ion

According to the x-ray structural analysis of $[Zr(H_2O)_2EDTA]$, Zr(IV) is surrounded by hexadentate EDTA and two water molecules corresponding to a zirconium coordination number of eight (25). The coordinated water can be replaced by more strongly binding molecules such as organic bidentate ligands (26). We followed the ternary complex formation of Zr-EDTA with fluoride ion by ^1H and ^{19}F NMR spectroscopy in D_2O solution. Figure 2 shows the ^{19}F NMR spectra of the solution containing equimolar amounts of $[Zr(CO_3)EDTA]^{2-}$ and fluoride ion at various pH ranges. The ^{19}F NMR chemical shift was expressed relative to the position of fluoride ion signal (NaF). Two peaks at 122.38 and 131.57 ppm were observed newly at pH 4.9 while the signal of free fluoride ion was not observed. The significant shift of ^{19}F peaks from the location of free fluoride ion can be attributed to the direct coordination of fluoride ion to Zr(IV). When the amount of fluoride ion is doubled as shown in Fig. 3, the peak at 131.57 ppm decreased significantly while the peak at 122.38 ppm increased. Therefore we assigned these peaks, i.e., at 131.57 and 122.38 ppm as the signals of mono and bis fluoride complexes, respectively. Obviously, the peak ratio between the free and the complexed fluoride ion depends on the pH while the peak position did not change practically. The peak intensity of the complexed fluoride relative to free fluoride decreased with the increase in pH. In other words, complexation of fluoride ion with the zirconium is unfavorable at higher pH region. The optimum pH for maximum peak ratio of complexed fluoride ranges from 3 to 6. Figure 4 shows the ^1H NMR spectra of $K_2[Zr(CO_3)EDTA]$ in the absence and presence of fluoride ion. The parent complex gave typical quartet peaks attributed to the AB pattern of the chelate acetate protons and a single peak of ethylene protons (17,27). When fluoride ion was present, new acetate AB quartet and ethylene peaks were observed in addition to the parent peaks. The observed new peaks can be attributed to the formation of mixed complex by the ligand exchange of CO_3^{2-} with fluoride ion.

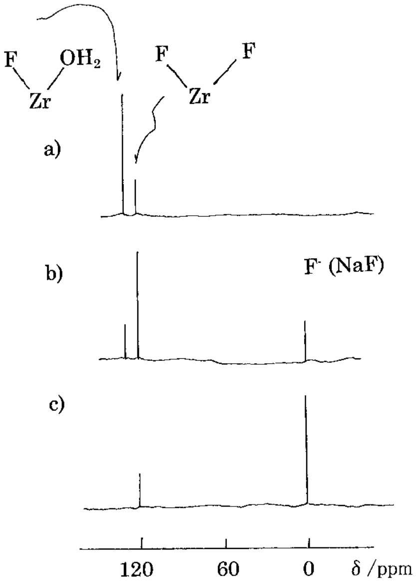


Figure 2. ^{19}F NMR spectra of NaF in the presence of an equimolar amount of $[Zr(CO_3)EDTA]^{2+}$ in D_2O; (a) pH = 4.9, (b) pH = 7.7, (c) pH = 9.0. The chemical shift is expressed relative to the signal of F^- of NaF.

Our observation by ^{1}H and ^{19}F NMR spectra suggests strongly that the direct complexation of fluoride ion on the metal is the most plausible mechanism as given in reactions (1) and (2). Complex formation of $[Zr(H_2O)_2EDTA]$ with fluoride ion was examined by potentiometric titration. The formation constants K_1 and K_2 of Eqs. (1) and (2) were determined and the numerical data are given in Table 2. The obtained values are in good agreement with a recent report (27,28).

$$K_1 = \frac{[[ZrF(H_2O)EDTA]^-]}{[[Zr(H_2O)_2EDTA]][F^-]} \tag{3}$$

$$K_2 = \frac{[[ZrF_2EDTA]^{2-}]}{[[ZrF(H_2O)EDTA]^-][F^-]} \tag{4}$$

Zr(IV) Complex of Polymer Chelating Resin

The potentiometric titration and NMR measurements in homogeneous solution suggested that Zr(IV) loaded chelating resins can retain fluoride ion

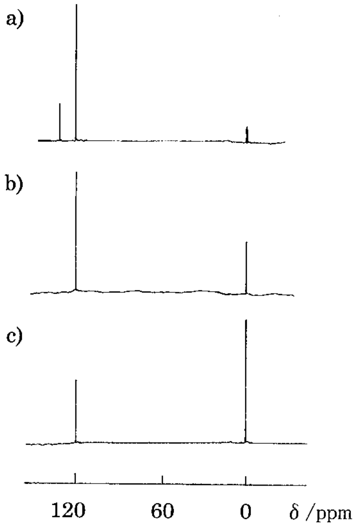


Figure 3. ^{19}F NMR spectra of 2:1 mixture of NaF and $[Zr(CO_3)\ EDTA]^{2+}$ in D_2O; (a)pH = 3.8, (b) pH = 6.3, (c) pH = 9.8.

by ternary complex formation. We have prepared the Zr(IV) complex of the CMA resin in which two sets of IDA are contained in analogy to $EDTAH_4$ along with the conventional chelating resin having IDA. Zr(IV) was loaded onto the present resins by treatment with 1 *M* hydrochloric acid solution. The zirconium content in the dry resin was found to be 0.82 and 0.54 mmol g^{-1} resin on an average for CMA and IDA resins, respectively. The Zr(IV) was retained firmly on the CMA resin, and the polymer complexes were stable over a wide pH range (pH > 1) as expected based on the significant stability of the Zr(IV)–EDTA complex (29).

Table 2. Ternary Complex Formation Constants of Fluoride Ion with $[Zr(H_2O)_2EDTA]$ in Water at 25°C

Log K_1	Log K_2
4.52	2.48

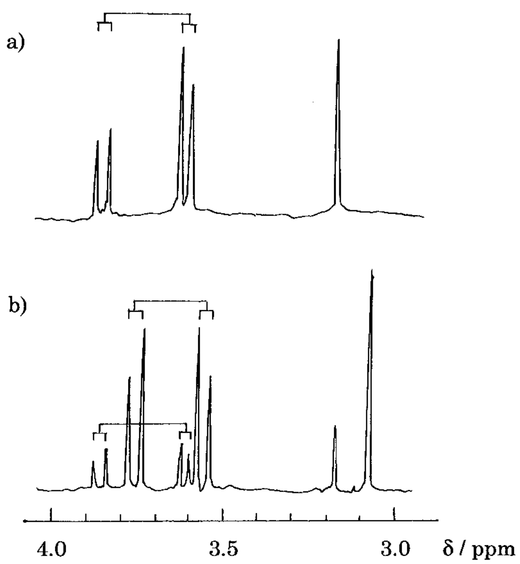


Figure 4. ^{1}H NMR spectra of $[Zr(CO_3)EDTA]^{2-}$ in the absence and presence of equimolar amounts of NaF in D_2O; (a) $[Zr(CO_3)\ EDTA]^{2+}$, (b) $[Zr(CO_3)\ EDTA]^{2+}$ and NaF (1:1) at pH 4.6.

Percent Extraction of Fluoride Ion

As we expected from the homogeneous system, both Zr-CMA and Zr-IDA resins retain fluoride ion readily at acidic–neutral pH region. Figure 5 shows the percent extraction of fluoride ion as a function of pH for the Zr-CMA and Zr-IDA resins. Almost complete extraction of fluoride ion was attained at pH ranging 3–5 in both resins, but the percentage decreases towards the higher pH region and no fluoride extraction occurred in strong alkaline media. Since neither the CMA resin nor the IDA resin itself retained fluoride ion, the extraction of fluoride ion was attributed to the ternary complex formation with loaded zirconium. The optimum condition for the removal of fluoride ion ranges from pH 3 to 5, which is consistent with that observed by the NMR study.

Adsorption Isotherm

The adsorption characteristics of fluoride ion with the Zr-CMA and Zr-IDA resins have been analyzed by using Langmuir model of adsorption (21,22). The

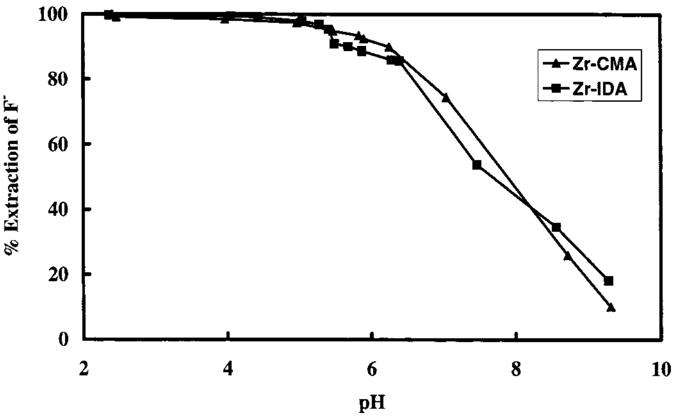


Figure 5. Percent extraction of fluoride ion as the function of pH. (σ) Zr-CMA resin, (■) Zr-IDA resin. Resin: 0.5 g, $[F^-]_{init.} = 2.87\,mM$, shaking time: 6 days at 25°C.

following Eq. (5) was used to determine the equilibrium constant (K) and the capacity of the resins (C_s),

$$\frac{C}{C_x} = \frac{1}{KC_s} + \frac{C}{C_s} \tag{5}$$

where C is the concentration of the fluoride ion in the solution (mmol dm^{-3}) and C_x is that in the resin at equilibrium (mmol g^{-1}). Plot of C/C_x against C for Zr-CMA and Zr-IDA resins gave a good straight line. The numerical results are given in Table 3. The binding constant and adsorption capacities of both the polymer complexes did not differ significantly. The adsorption capacities of these resins for fluoride ion were obviously much higher than Zr(IV) contents. This suggests that the Zr(IV) complex can capture up to two fluoride ions and it agrees with the fluoride complex formation in homogeneous solution.

Table 3. Langmuir Data for the Adsorption of Fluoride Ion with Zr-CMA and Zr-IDA Resins at pH 5.0 and 25°C

Resin	C_s (mmol g^{-1})	Log K	Regression
Zr-CMA	1.15	3.69	0.997
Zr-IDA	1.05	3.80	0.998

Effect of Diverse Ions

Since industrial wastewater tends to contain common background ions, the influence of such anions towards fluoride ion adsorption was also investigated. Figure 6 shows the percent extraction of fluoride ion for the Zr-IDA and Zr-CMA resins in the presence of various concentrations of diverse ions. Most of the anions, except $H_2PO_4^-$, did not interfere with the adsorption of fluoride ion in the presence of up to 100 times the fluoride concentration. The high selectivity of the Zr-loaded chelating resins for fluoride ion cannot be interpreted simply by ion

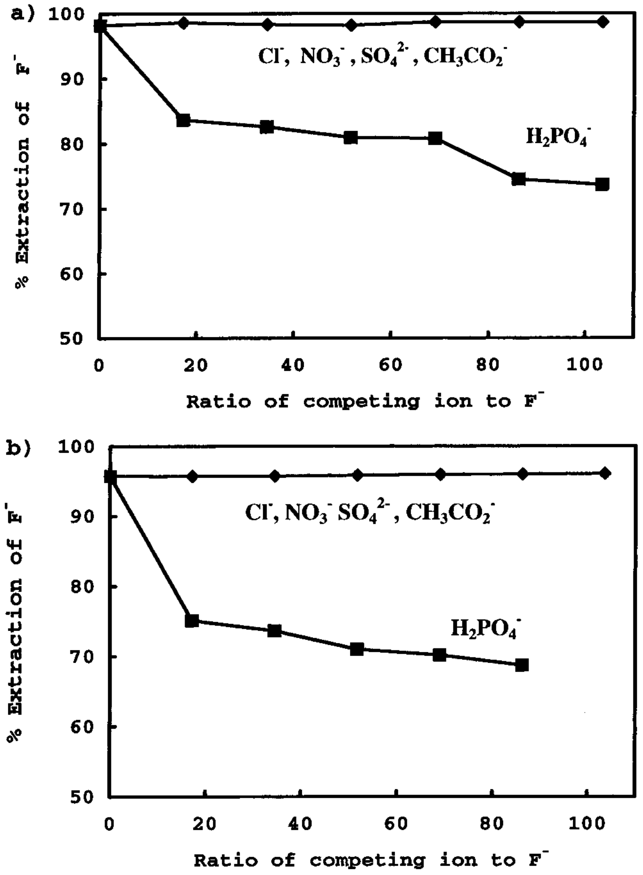


Figure 6. Effect of diverse ions on the percent extraction of fluoride ion. (a) Zr-IDA resin, (b) Zr-CMA resin. Resin: 0.5 g, $[F^-] = 2.87\,mM$, pH = 5.0, shaking time 6 days at 25°C.

exchange mechanism, which is based on the electrostatic attraction force. Direct coordination of fluoride takes place most likely in the polymer Zr(IV) complex systems in analogy to the homogeneous complex.

Kinetic Study

Although equilibrium study is of fundamental importance in characterizing the performance of the adsorption system, the rate of adsorption is extremely important from a practical point of view. The time course for the adsorption of fluoride ion on the Zr-CMA and Zr-IDA resins was monitored at pH 5. Vermeulen's approximation (23,24) was applied to obtain the overall rate constant (k)

$$\ln(1 - A^2) = -kt \tag{6}$$

where $A = [F]_t/[F]_{eq}$, $[F]_t$ is fluoride ion retained in the resin at the given time t and $[F]_{eq}$ is that in the resin at equilibrium. Figure 7 shows plots of $\ln(1 - A^2)$ against time for the two resins. A good linear correlation was obtained in both cases indicating that the kinetic equation adopted is valid in these systems. The rate-determining step appears to be the particle-diffusion process (23). The

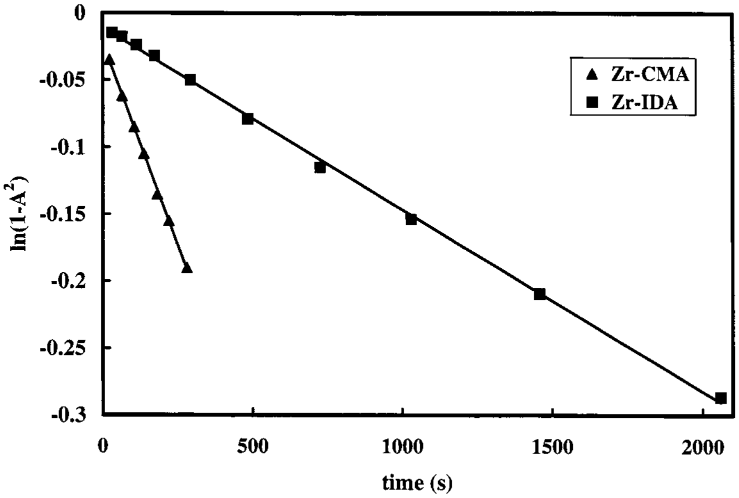


Figure 7. Kinetic study of the adsorption of fluoride ion by (▲) Zr-CMA resin and (■) Zr-IDA resin. Resin: 4 g, $[F]_{init.}$: 110 ppm for Zr-IDA resin, 214 ppm for Zr-CMA resin, volume of solution: 300 cm^3, pH = 5, stirring speed 400 rpm, temperature 25°C.

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Table 4. Kinetic Data for the Adsorption Of Fluoride Ion with Zr-CMA and Zr-IDA Resins at pH 5.0 and 25°C

Resin	k (sec^{-1})	Regression	Half life, $t_{1/2}$ (min)
Zr-CMA	6.02×10^{-4}	0.999	8.0
Zr-IDA	1.35×10^{-4}	0.999	35.5

kinetic data listed in Table 4 indicate that the reaction rate of fluoride ion uptake with Zr-CMA resin is more than four times faster than that with Zr-IDA resin. This could be interpreted by the difference in relative locations of the hydrophilic coordination site and hydrophobic polymer matrix in the two resins. The Zr(IV) as the active site in the Zr-CMA resin is located relatively remote from the polymer matrix due to the presence of diethylenetriamine moiety, whereas that in the Zr-IDA group is spaced only by a methylene group. Another remarkable difference of these two chelating resins is the dentate number of their metal binding group. The functional group of the CMA resin can form 1:1 octahedral complex with Zr(IV), whereas two sets of ligand groups are required for the IDA resin. Formation of such 1:2 complex must be restricted within the solid resin phase, and hence Zr-IDA resin involves coordinately unsaturated Zr(IV) moieties. This structural difference of complexes may affect the kinetics of ternary complex formation with fluoride ion.

Column Adsorption of Fluoride Ion

An attempt was made to demonstrate the adsorption of fluoride ion with Zr-CMA and Zr-IDA resins, i.e., the removal of fluoride ion in the continuous column system. Figure 8 shows the breakthrough curve for the adsorption of fluoride ion (10 ppm, acetate buffer) at different feed rates of solution. Obviously, the feed rate affected the adsorption efficiency of fluoride ion significantly. It is observed that the fluoride ion outside the column was less than 0.5 ppm upon passing up to 330 and 70 bed volumes for the Zr-CMA resin and Zr-IDA resin, respectively, under the flow rate of less than 0.5 $\text{cm}^3\,\text{min}^{-1}$. However, increase in feed rate resulted in a much earlier leakage of fluoride ion. Considering that the experimental condition and Langmuir's equilibrium data are similar to each other for the two adsorbents, the superior column performance of the Zr-CMA is attributed mainly to its faster adsorption rate. The fluoride ion retained was released from the resins by passing 1 M NaOH solution through the column. The recovery of fluoride ion ranged 97–98% for both resins. The column was used repeatedly upon washing with water, rinsing with 0.2 M acetate buffer (pH = 4.5)

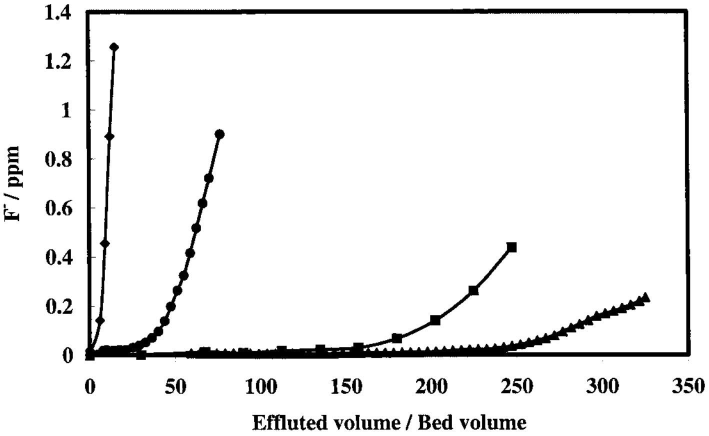

Figure 8. Column breakthrough profile for the adsorption of fluoride ion by the Zr-IDA resin and Zr-CMA resin at different feed rates. (◆) Zr-IDA resin ($0.70\,cm^3\,min^{-1}$, EBCT = 11 min), (●) Zr-IDA resin ($0.55\,cm^3\,min^{-1}$, EBCT = 14 min). (■) Zr-CMA resin ($0.70\,cm^3\,min^{-1}$, EBCT = 12.7 min), (▲) Zr-CMA resin ($0.50\,cm^3\,min^{-1}$, EBCT = 17.8 min). Resin 4 g, $[F^-]_{feed} = 10$ ppm, pH = 5 (acetate buffer). EBCT denotes the empty bed contact time (resin bed volume/flow rate).

followed by washing with water. We have demonstrated that the column performance of the Zr-CMA resin did not change for at least five adsorption and regeneration cycles. However, when we supply a very high concentration of fluoride ion continuously, gradual leaking of zirconium from the column as zirconium fluoride takes place inevitably.

In another experiment, we added fluoride ion into seawater so as to be 10 ppm and the solution was passed through the Zr-CMA resin column. No appreciable interference from high concentrations of chloride and other ions was observed and the fluoride ion was retained selectively on the column.

CONCLUSION

According to the ^{19}F and ^{1}H NMR spectroscopies, it was suggested strongly that Zr(IV)–EDTA complex can capture up to two fluoride ions by direct coordination to Zr(IV) center. The equilibrium constants of ternary complex formation of fluoride and Zr(IV)–EDTA were determined by potentiometry. The Zr(IV) complexes of polymer having EDTA and IDA homologues were prepared and their adsorption characteristics were examined. The optimum pH for the adsorption of the fluoride ion with the Zr-CMA and Zr-IDA resins were in the pH ranging 3–5. Common anions including chloride, nitrate, sulfate, and acetate did not interfere with the adsorption of fluoride ion in their presence up to hundred times in concentration, while phosphate ion affected the fluoride adsorption significantly. The reaction rate of fluoride ion with Zr-CMA is more than four times faster than that of Zr-IDA resin. The column performance of the Zr-CMA resin is superior to that of the Zr-IDA resin presumably due to rapid kinetics of the former resin. Columns were used repeatedly for adsorption and regeneration cycles. Although improvement of the resin performance is necessary for the practical application inevitably, we have proposed the effectiveness of the polymer resin involving Zr–EDTA homologue for the selective removal of fluoride ion.

ACKNOWLEDGMENTS

Sunamani Kerketta is grateful to Japan International Cooperation Agency for the financial support during his stay in TNIRI on leave from Ministry of Environment and Forest, Eastern Region, Bhubaneswar, Orissa, India.

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Received August 2000

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