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Separation of fluoride from aqueous solution by electrodialysis: Effect of process parameters and other ionic species

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Abstract

Removal of fluoride from aqueous solution by electrodialysis was studied. Applied voltage, feed flow rate, fluoride concentration in the solution and effect of the other anions as sulfate, chloride were investigated as experimental parameters on fluoride removal from aqueous solution. The separation performance was evaluated in terms of mass transfer and energy consumption. It was obtained that the separation performance increased when the initial concentration of fluoride in the feed solution increased. Percent removal of fluoride increased as the applied potential increased. However, the effect of feed flow rate was not apparent in the range of applied feed flow rate. Separation of fluoride was influenced by chloride but not by sulfate ions.

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1. Introduction

Fluoride in the environment occurs through natural presence in the earth's crust and industrial activities, especially, semiconductor, electroplating, aluminum, glass, ceramic and fertilizers industries [1,2]. The discharge of such wastewater leads to the fluoride contamination of surface and ground water. The optimum fluoride ion level in drinking water for general good health is considered to be between 0.5 and 1.0 mg/L [3]. The optimum fluoride level in drinking water for general good health set by WHO is considered to be between 0.5 and 1.0 mg/L [4]. US EPA recently established a discharge standard of 4 mg/L for fluoride from wastewater treatment plant. Beijing is working toward this standard value although the national fluoride discharge standard for industrial wastewater is 10 mg/L in China [5]. High concentrations of fluoride in drinking water result in fluorosis (dental/skeletal abnormalities) and several neurological damages in severe cases.

Various treatment technologies based on precipitation [6], ion exchange [7–9], adsorption [10–12], and membrane process

0304-3894/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2007.08.024 such as reverse osmosis [13,14], nanofiltration [15], Donnan dialysis [16] and electrodialysis [17,18] have been suggested for fluoride removal. Most methods for the fluoride removal suffer from one of the following drawbacks: high initial cost, lack of selectivity, low capacity, and complicated or expensive regeneration. Of the many membrane processes available for the separation of ions from solutions, only two, reverse osmosis (RO) and electrodialysis (ED), have reached the practical application stage for the removal of inorganic contaminants from drinking water and wastewater. Both processes remove salts from seawater and brackish water and thus are commonly classified as desalination processes [19].

The electrodialysis is a widely used electro-membrane process especially for desalination of brackish water and sodium chloride recovery from seawater. The removal of ionic components from aqueous solution through ion exchange membranes is carried out under the driving force of an electrical field [20]. When a direct current potential is applied between two electrodes, the positively charged cations move to the cathode, passing through the negatively charged cation exchange membrane and retained by the positively charged anion exchange membrane. While the negatively charged anions move to the anode, passing through the anion exchange membrane and retained by the cation exchange membrane. At the end,

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ion concentrations increase in alternate compartments with a simultaneous decrease of ions in other compartments [21,22]. Previously, we studied the separation performances of monovalent and divalent salts by electrodialysis as a function of applied voltage, flow rate, and pH [23–26]. Elsewhere, separations of Na⁺, K⁺, Ca²⁺ and Mg²⁺ ions from ternary mixtures prepared from NaCl–CaCl₂ and KCl–MgCl₂ mixtures were investigated by the electrodialysis (ED) method using batch mode of operation as a function of solution concentration, applied voltage and flow rate [27]. In addition, separation of monovalent (Na⁺, K⁺) and divalent ions (Ca²⁺, Mg²⁺) from unary and binary mixtures by electrodialysis were compared using various salt combinations (NaCl, NaNO₃, KCl, KNO₃, K₂SO₄, Na₂SO₄, CaCl₂, Ca(NO₃)₂, MgCl₂, Mg(NO₃)₂) [28].

The interest in using electrodialysis processes to remove excess fluoride from drinking water has increased world wide principally because it is a simple process and does not have many of the defects of chemical processes [29]. Some studies were conducted to reduce fluoride by electrodialysis from brackish water and it was demonstrated that electrodialysis is a reasonable process for removing fluoride from brackish water. Because of higher concentration of bivalent salts in the brackish water, the risk of precipitation of these salts, especially sulfate and carbonate in the concentrate compartment by exceeding solubility, became very important. The membranes can be damaged by scaling and fouling. To avoid these risks, the ED operation was carried out according to two methods as without and with a chemical pretreatment. Without pretreatment, ACS-CMX membranes were used especially to stop the transport of bivalent anions in order to prevent the possible precipitation of bivalent salts. ACS membrane transports the anions in the following order $Cl^- > F^- > HCO_3^- > SO_4^{2-}$. As the second method, before ED operation, a chemical pretreatment of the brackish water was carried out to precipitate the calcium ions. Since this method requires chemical additives in the pretreatment step, it has more impact on the environment than the first one [17,30]. Recently, removal of fluoride from underground brackish water was studied by adsorption on natural chitosan and by ED [31]. Another study was reported on removal of fluoride and nitrate removal from groundwater by ED [32].

Types of co-existing anions play important roles in defluoridation in ED process. The aim of this study is to elucidate the effects of various co-existing anions on defluoridation in ED process. Two kinds of common anions, chloride and sulfate, were tested to discern the effects of different co-existing anions. In addition, the effects of process parameters such as applied voltage, flow rate and initial fluoride feed concentration were investigated.

2. Experimental

TS-l-l0 electrodialysis equipment (Tokuyama) was employed for experimental studies. A schematic view of the experimental set-up is shown in Fig. 1. This equipment contains a stack with 10 pairs of Neosepta[®] CMX (cation exchange) and AMX (anion exchange) membranes providing for each a membrane area of 1 dm², respectively. A rectifier is provided to supply a DC



Fig. 1. Batch-mode operation of electrodialysis system.

power at constant voltage (max. 18 V) or constant current (max. 3 A). Three pumps have capacities of max. 1.8 L/min. Three solution tanks (each 1 L) are used for holding the diluted, the concentrated, and the electrode rinse solutions. The electrodes are platinum plated titanium (anode) and stainless steel (cathode) [33]. When a direct current potential is applied, fluoride ions migrates towards the anode. Fluoride ions leave the dilute compartment and move through the anion exchange membrane and retained by the cation exchange membrane in the concentrate compartment. Samples were taken periodically from dilute and concentrate compartments. The batch tests were carried out with NaF solutions prepared in deionized water at different concentrations (25, 50, 75, 100, 200 mg F/L) and using various potentials (5, 7 and 10 V) and flow rates (0.8, 1.2 and 1.6 L/min). The solutions of sulfate and chloride were prepared through the dissolution of Na₂SO₄ and NaCl in deionized water. The concentrations of anions were determined by ion chromatography (Shimadzu LC 10 Ai).

3. Results and discussion

3.1. Effect of initial feed concentration on separation performance

The effect of initial feed concentration on separation performance of fluoride from aqueous solution was investigated using aqueous solutions at various concentrations of fluoride. Before performance tests, limiting current measurement were carried out for each concentration. The applied currents were changed keeping the solution concentration constant. The feed and permeate solutions pumped from the same reservoir were circulated through the feed and permeate compartments, respectively, and then recycled to the reservoir at a flow rate of 0.8 L/min. By doing this way, the solution concentration in the feed could be maintained constant at a desired level during the experiments. If the applied current is changed, obtained potential values will change linearly until limiting current point has been reached. After this point, there is a sharp change in slope. This switch-

 Table 1

 Applied potential values for various feed concentrations

Initial concentration (mg F/L)	Applied potential (V)	
25	7.50	
50	7.53	
75	10.05	
100	10.23	
200	10.50	

ing point was determined as limiting current point. Table 1 shows the voltage values applied for each concentration values of fluoride.

Histories of change in fluoride ion concentration at any time over initial feed concentration (C/C_0) using different initial concentration of fluoride are given in Fig. 2. The concentrated (C) and dilute (D) streams were monitored for fluoride ion concentration, current and conductivity values by time. Fluoride ion concentrations of dilute and concentrated stream were measured at certain time intervals until the operation time needed for reaching 0.01 A. The changes in fluoride concentration and current in dilute compartment versus time plots are given in Figs. 3 and 4, respectively as a function of fluoride concentration in the feed. These figures fit to each other well. It was seen that the lowest concentration of fluoride was reached at a longer period as the initial concentration of fluoride in the feed solution increased (Fig. 3). It was obtained that the percent removal of fluoride increased when the initial concentration of fluoride in the feed solution increased owing to the increased conductivity of fluoride ions in a solution having a high ionic strength. But, total process time increased with increasing initial fluoride concentration in the feed.

3.2. Effect of voltage on separation performance

The effect of voltage on fluoride removal was investigated at a constant feed flow rate of 1.6 L/min and room temperature.



Fig. 2. Effect of initial fluoride concentration on the separation of fluoride by ED (D: dilute, C: concentrated streams, voltages applied: 7.50 V (25 mg F/L), 7.53 V (50 mg F/L), 10.05 V (75 mg F/L), 10.23 V (100 mg F/L), 10.50 V (200 mg F/L), feed flow rate: 1.6 L/min, $T: 25 ^{\circ}\text{C}$).



Fig. 3. Concentration vs. time plots for dilute stream as a function of initial fluoride concentration (see Fig. 2 for experimental conditions).



Fig. 4. Current vs. time plots for dilute stream as a function of initial fluoride concentration (see Fig. 2 for experimental conditions).

Initial feed concentration was 100 mg F/L-solution. Dimensionless form of concentration changes in dilute and concentrate compartments versus time graphs are shown in Fig. 5 while the respective current changes versus time plots are given in Fig. 6. The operation time needed for reaching 0.01 A becomes



Fig. 5. Effect of applied voltage on the separation performance of fluoride by ED (D: dilute, C: concentrated streams, F: 100 mg/L, feed flow rate: 1.6 L/min, $T: 25 \,^{\circ}$ C).



Fig. 6. Current vs. time plots in dilute stream as a function of applied potential (see Fig. 5 for experimental conditions).

much shorter and percent removal of fluoride increased when the applied potential increased.

3.3. Effect of feed flow rate on separation performance

The operation was carried out using different feed flow rates (0.8, 1.2, 1.6 L/min) and with a fluoride solution of 100 mg F/L. The operation was performed at a voltage of 10 V and at room temperature. As seen in Figs. 7 and 8, flow rate did not have an important effect on fluoride removal in the range of flow rates studied. It was not possible to increase the flow rate above 1.6 L/min since the maximum capacity of the pumps in the present system are defined as 1.8 L/min.

3.4. Effect of other ions on separation of fluoride

In the presence of chloride and sulfate ions, separation of fluoride by electrodialysis was investigated. The experiments were conducted with fluoride (100 mg F/L-solution) paired only with either chloride or sulfate and mixtures containing both chloride and sulfate ions. The ratios of equivalent concentrations of ionic



Fig. 7. Effect of feed flow rate on the separation performance of fluoride (D: dilute, C: concentrated streams, F: 100 mg/L, T: $25 \degree$ C).



Fig. 8. Current vs. time plots in dilute stream as a function of feed flow rate (see Fig. 7 for experimental conditions).

species in the mixture were adjusted as (1:1) in binary mixtures (F:Cl and F:SO₄) or (1:1:1) in ternary mixture (F:Cl:SO₄). Effect of other ionic species on separation of fluoride was shown in Figs. 9–11. The respective current changes for the case of binary and ternary mixtures in dilute streams were given in Fig. 12. It was obtained that the competition between fluoride and chloride ions was certain (Fig. 9). On the other hand, separation of fluoride was more rapid than that of sulfate ions (Fig. 10). When analyzed Fig. 11, one can see that the slope of the first segment of the fluoride curve is low because mainly chloride ions removed in 8 min. Next, when about 90% of chloride was removed, the slope of fluoride curve increased and at 16 min about 98% of fluoride was removed from the solution. After removal of fluoride, the slope of sulfate ion curve increased.

Percent removal of monovalent anions was higher than from the salt solutions containing divalent anions (sulfate). The anionic and cationic membranes have a typical selectivity for different ions such that divalent ions are more strongly retained in the membrane material and thus are thought to be transported



Fig. 9. Separation of fluoride from a binary mixture (F:Cl) (D: dilute, C: concentrated streams, F: 100 mg/L, Cl: 186 mg/L, voltage applied: 10.21 V, feed flow rate: 1.6 L/min, *T*: $25 \degree$ C).



Fig. 10. Separation of fluoride from a binary mixture (F:SO₄) (D: dilute, C: concentrated streams, F: 100 mg/L, SO₄: 252 mg/L, voltage applied: 9.66 V, feed flow rate: 1.6 L/min, *T*: 25 °C).



Fig. 11. Separation of fluoride from a ternary mixture (F:Cl:SO₄) (D: dilute, C: concentrated streams, F: 100 mg/L, Cl: 186 mg/L, SO₄: 252 mg/L, voltage applied: 9.51 V, feed flow rate: 1.6 L/min, *T*: 25 °C).

more slowly because of increasing hydratized radius of ions and ion charges. The ion size may have an additional effect: the larger the ion, the more its transport through the membrane is sterically hindered. When the hydratized radii of ions were compared, it



Fig. 12. Current vs. time plots for dilute stream regarding binary (F:Cl and F:SO₄) and ternary (F:Cl:SO₄) mixtures. (see Figs. 9-11 for experimental conditions).

Table 2			
Hydratized	radii	of	ions

Ionic species	Hydratized radius (A)
Chloride	3.32
Fluoride	3.52
Sulfate	3.79



Fig. 13. Effect of applied potential on the specific power consumption (F: 100 mg F/L, feed flow rate: 1.6 L/min, $T: 25 \degree$ C).

was seen that the order of hydratized radii followed the order of $Cl^- < F^- < SO_4^{2-}$ (Table 2). This finding agreed well with the reported literature [27,28,34,35].

3.5. Specific power consumptions

Specific power consumption can be described as the energy needed to treat unit volume of solution. The effects of operating parameters (applied voltage and feed flow rate) on specific power consumption (SPC) were studied. SPC was calculated using the following equation:

$$SPC = \frac{E \int_0^t I(t) dt}{V_D}$$

where E is the applied potential, I the current, V_D the dilute stream volume and t is the time. The calculated SPC values for each potential and feed flow rate for 100 mg F/L-solution



Fig. 14. Effect of feed flow rate on the specific power consumption (F: 100 mg F/L, applied voltage: 10.23 V, T: $25 \degree$ C).

Table 3Effect of ionic species on SPC values

Solution	SPC (Wh/L)	
F-	0.17	_
$F^- + Cl^-$	0.32	
$F^{-} + SO_4^{2-}$	0.33	
$F^{-} + SO_4^{2-} + Cl^{-}$	0.49	

Table 4

SPC values at various feed concentrations

Initial feed concentration (mg F/L)	SPC (Wh/L)	
25	0.02	
50	0.05	
75	0.12	
100	0.17	
200	0.33	

are given in Figs. 13 and 14, respectively. SPC was remarkably affected by the change in applied potential. It was obtained that the specific power consumption increased when higher voltage is applied for 100 mg F/L. There is no any considerable effect of flow rate on the SPC.

As summarized in Table 3, SPC values increased as the number of ionic species in the solution increased. Table 4 summarizes the SPC values calculated for various initial concentrations of fluoride. According to the results obtained, one could conclude that power consumption increased with increasing initial concentration of fluoride in the solution.

4. Conclusions

Electrodialysis is an effective method for removal of excess fluoride from water or wastewater. On the other hand, the electrodialysis process was more effective when the initial concentration of fluoride in the feed is high if fluoride is the only anionic specie in water. The operation time for fluoride removal became shorter when applied potential increased. The competition between fluoride and chloride ions was much greater than the competition between fluoride and sulfate ions.

The effect of initial concentration of fluoride on fluoride removal by ED will be studied in the presence of other anionic species such as chloride and sulfates for the next step of our research. The results will be published elsewhere.

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References

- M.G. Sujana, R.S. Thakur, S.B. Rao, Removal of fluoride from aqueous solution by using alum sludge, J. Colloid Interface Sci. 206 (1998) 94–101.
- [2] A. Toyoda, T. Taira, A new method for treating fluorine wastewater to reduce sludge and running costs, IEEE Trans. Semiconduct. Manufact. 13 (3) (2000) 305–309.

- [3] Y. Wang, E.J. Reardon, Activation and regeneration of a soil sorbent for defluoridation of drinking water, Appl. Geochem. 16 (2001) 531–539.
- [4] S. Ghorai, K.K. Pant, Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina, Sep. Purif. Technol. 42 (2005) 265–271.
- [5] F. Shen, X. Chen, P. Gao, G. Chen, Electrochemical removal of fluoride ions from industrial wastewater, Chem. Eng. Sci. 58 (2003) 987–993.
- [6] N. Mameri, A.R. Yeddou, H. Lounici, D. Belhocine, H. Grib, B. Bariou, De fluorination of septentrional Sahara water of North Africa by electro coagulation process using bipolar aluminum electrodes, Water Res. 32 (5) (1998) 1604–1612.
- [7] K.M. Popat, P.S. Anand, B.D. Dasare, Selective removal of fluoride ions from water by the aluminum form of the aminomethylphosphonic acid-type ion exchanger, React. Polym. 23 (1994) 23–32.
- [8] N. Kabay, H. Kodama, Ion exchange properties of BiO(NO₃)·0.5H₂O towards fluoride ion in solution, Solv. Extr. Ion Exch. 18 (3) (2000) 583–603.
- [9] H. Kodama, N. Kabay, Reactivity of inorganic anion exchanger BiPbO₂(NO₃) with fluoride ions in solution, Solid State Ionics 141/142 (2001) 603–607.
- [10] C.L. Yang, R. Dluhy, Electrochemical generation of aluminum sorbent for fluoride adsorption, J. Hazard. Mater. B 94 (2002) 239–252.
- [11] S. Ghorai, K.K. Pant, Investigations on the column performance of fluoride adsorption by activated alumina in a fixed-bed, Chem. Eng. J. 98 (2003) 165–173.
- [12] Y. Zhou, C. Yu, Y. Shan, Adsorption of fluoride from aqueous solution on La³⁺-impregnated crosslinked gelatin, Sep. Purif. Technol. 36 (2004) 89–94.
- [13] B.E. Smith, Desalting and groundwater management in the San Joaquin valley, Desalination 87 (1992) 151–174.
- [14] S. Bouguecha, M. Dhahbi, The role of membrane technologies in supplying drinking and industrial water in Tunisia: conventional process and new trends, Desalination 151 (2002) 75–86.
- [15] K. Hu, J.M. Dickson, Nanofiltration membrane performance on fluoride removal from water, J. Membr. Sci. 279 (2006) 528–529.
- [16] E. Kir, E. Alkan, Fluoride removal by Donnan dialysis with plasmamodified and unmodified anion-exchange membranes, Desalination 197 (2006) 217–224.
- [17] Z. Amor, B. Bariou, N. Mameri, M. Taky, S. Nicolas, A. Elmidaoui, Fluoride removal from Corn brackish water by electrodialysis, Desalination 133 (2001) 215–223.
- [18] M. Tahaikt, I. Achary, M.A. Menkouchi Sahli, Z. Amor, M. Taky, A. Alami, A. Boughriba, M. Hafsi, A. Elmidaoui, Defluoridation of Moroccan ground water by electrodialysis: continuous operation, Desalination 167 (2004) 357–365.
- [19] D. Clifford, S. Subramonian, T.J. Sorg, Water treatment processes. III. Removing dissolved inorganic contaminants from water, Environ. Sci. Technol. 20 (11) (1986) 1072–1080.
- [20] F. Hell, J. Lahnsteiner, H. Frischherz, G. Baumgartner, Experience with full-scale electrodialysis for nitrate and hardness removal, Desalination 117 (1998) 173–180.
- [21] H. Strathmann, Electrodialysis, in: W.S. Winston Ho, K.K. Sirkar (Eds.), Membrane Handbook, Van Nostrand Reinhold, New York, 1992.
- [22] H. Strathmann, in: P.M. Bungay, H.K. Lonsdale, M.N. de Pinho (Eds.), Synthetic Membranes: Science and Applications, Reidel, Dordrecht, 1986.
- [23] M. Demircioglu, N. Kabay, E. Ersoz, I. Kurucaovali, C. Safak, N. Gizli, Cost comparison and efficiency modeling in the electrodialysis of brine, Desalination 136 (2001) 317–323.
- [24] N. Kabay, M. Demircioğlu, E. Ersöz, I. Kurucaovali, Removal of calcium and magnesium hardness by electrodialysis, Desalination 149 (1–3) (2002) 343–349.
- [25] M. Demircioglu, N. Kabay, I. Kurucaovali, E. Ersoz, Demineralization by electrodialysis (ED)-separation performance and cost comparison for monovalent salts, Desalination 153 (1–3) (2002) 329–333.
- [26] N. Kabay, M. Arda, I. Kurucaovali, E. Ersoz, H. Kahveci, M. Can, S. Dal, Ş. Kopuzlu, M. Haner, M. Demircioglu, Effect of feed characteristic on separation performances of monovalent and divalent salts by electrodialysis, Desalination 158 (1–3) (2003) 95–100.

- [27] N. Kabay, H. Kahveci, Ö. İpek, M. Yüksel, Separation of monovalent and divalent ions from binary mixtures by electrodialysis, Desalination 198 (2006) 74–83.
- [28] N. Kabay, Ö. İpek, H. Kahveci, M. Yüksel, Effect of salt combination on separation of monovalent and divalent salts by electrodialysis, Desalination 198 (2006) 81–94.
- [29] M. Zeni, R. Riveros, K. Melo, R. Primieri, S. Lorenzini, Study on fluoride reduction in artesian well-water from electrodialysis process, Desalination 185 (2005) 241–244.
- [30] Z. Amor, S. Malki, M. Taky, B. Bariou, N. Mameri, A. Elmidaoui, Optimization of fluoride removal from brackish water by electrodialysis, Desalination 120 (1998) 263–271.
- [31] M.A. Menkouchi Sahlia, S. Annouarb, M. Tahaikt, M. Mountadar, A. Soufianec, A. Elmidaoui, Fluoride removal from underground brackish water by

adsorption on the natural chitosan and by electrodialysis, Desalination 212 (2007) 37–45.

- [32] L.J. Banasiak, T.W. Kruttschnitt, A.I. Sschafer, Desalination using electrodialysis as a function of voltage and salt concentration, Desalination 205 (2007) 38–46.
- [33] Neosepta-Ion Exchange Membranes Information Brochure, SEC System Dept., Tokuyama Corp., Tokyo, Japan, 1999.
- [34] K.E. Bouhidel, M. Rumeau, Comparison of the electrodialytic properties of NiSO₄ and NiCl₂: influence of the salt nature in electrodialysis, Desalination 132 (2000) 195–197.
- [35] R.S. Gartner, F.G. Wilhelm, G.J. Witkamp, M. Wessling, Regeneration of mixed solvents by electrodialysis: selective removal of chloride and sulfate, J. Membr. Sci. 250 (2005) 113–133.