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Separation of Low Concentration of Fluoride from Water by Electrodialysis (ED) in the Presence of Chloride and Sulfate Ions

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Abstract: Removal of low concentration of fluoride (2 mg F^-/L) in the presence of chloride and sulfate ions from aqueous solution by electrodialysis was studied. The equivalent ratios of sulfate and/or chloride were investigated as co-existing ions 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 equivalent ratios of chloride to fluoride and sulfate to fluoride were increased. After 13 min of operation time, 63% of fluoride was removed from the solution when a binary mixture of $F^- : Cl^-$ (1 : 25) was employed. In the case of a binary mixture of $F^- : SO_4^{2-}$ (1 : 25), removal of fluoride was 93% in 16 min. For a ternary mixture of $F^- : Cl^- : SO_4^{2-}$ (1 : 25 : 25), fluoride was separated from the mixture with a 96% of removal in 20 min.

Keywords: Chloride, electrodialysis, fluoride, ion exchange membrane, specific power consumption, sulfate, water, water treatment

INTRODUCTION

Fluoride occurs naturally in soil, water, plants, and animals in trace quantities. In groundwater, natural fluoride concentrations range from trace quantities to over 25 mg/L. When fluoride is ingested by humans and other animals, some is taken up by body tissues with long-term

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deposition in teeth and bones (1). Low concentrations of fluoride in drinking water have been considered beneficial to prevent dental carries. It has long been known that chronic intake of excessive fluoride ($>1\,mg/L$) can lead to severe dental and skeletal fluorosis. It does not only affect teeth and skeleton, but its accumulation over a long period can also lead to change in the DNA structure (2). 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).

Various treatment technologies based on precipitation (4–6), ion exchange (7,8), adsorption (9–11), and membrane processes such as reverse osmosis (12–14), nanofiltration (15,16), Donnan dialysis (17–19), and electrodialysis (20–22) have been applied for fluoride removal from water. 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. The interest in using the electrodialysis process to remove excess fluoride from water has increased worldwide because it is a simple process and does not request any chemicals for regeneration step.

Electrodialysis (ED) is an electrochemical process for the separation of ions across charged membranes from one solution to another under the influence of electrical potential difference. This process has been widely applied to treat brackish water for potable use or to desalt and concentrate effluents for reuse (23).

The interest in using electrodialysis processes to remove excess fluoride from drinking water has increased world wide principally because it is rather a simple process and does not cause problems during the process applications (20). Elmidaoui et al., performed a study to evaluate the cost of fluoride removal by electrodialysis on the basis of industrial and economic data (24).

Tahaikt et al. performed a continuous electrodialysis operation for defluoridation of groundwater. The performances of two anion exchange membranes, NEOSEPTA ACS and AXE 01, were compared and the optimal operating conditions for the best membrane were determined. They obtained good results with ACS membrane because of its best fluoride rejection and poor sulfate rejection (25).

Amor et al. used ED operation to remove fluoride from brackish water. The behavior of water parameters has been followed and optimal operational conditions for obtaining desired potable water from fluoride rich brackish water have been proposed. The results showed that a desired product water quality can easily be obtained by ED (26).

In our previous work, we studied on fluoride removal by ED at a concentration range of 25–200 mg F^-/L. It was obtained that percent removal of fluoride ion by ED increased when the initial concentration of fluoride was high due to the increased conductivity of the solution at high ionic strength. In addition, the separation of fluoride from the binary (F-Cl or F-SO_4) and ternary (F-Cl-SO_4) mixtures was investigated (20). The aim of this study is the remove the fluoride from a mixture containing fluoride at low concentration (2 mg F^-/L) in the presence of co-existing ions such as chloride and sulfate.

EXPERIMENTAL

TS-1-10 batch-type ED unit (Tokuyama Co., Japan) was used for experimental studies. The ED stack contained 10 cells which include 10 pairs of anion and cation exchange Neosepta CMX (strongly acidic cation exchange) and AMX (strongly basic cation exchange) membranes having effective membrane areas of 1 dm^2. A DC power supply at constant voltage (max. 18 V) or constant current (max. 3A) and three pumps with max. 1.8 L/min capacities were provided. Three solution tanks with a volume of 1 L each were used for holding the diluted, the concentrated and the electrode rinse solutions. The electrodes are platinum plated (anode) and stainless steel (cathode) (27).

All reagents were of analytical grade and high quality ultra pure water was used for preparing all solutions. Samples were taken periodically from diluted and concentrated compartments. The batch tests were carried out with NaF solutions prepared in deionized water with 2 mg F^-/L concentration. The solutions of sulfate and chloride were prepared through the dissolution of Na_2SO_4 and NaCl in deionized water. The concentrations of chloride and sulfate anions were determined by ion chromatography (Shimadzu LC 10 A*i*). The analysis of fluoride was performed with an ion selective electrode system F-ISE (WTW F800 Fluoride Combination Electrode) connected to the WTW inoLab pH/ION 735 ionmeter. The problems with ion selective electrode measurements are the effect of interferences due to the presence of other ions in solution. TISAB (WTW Total Ionic Strength Adjustment Buffer) solution which contains glacial acetic acid, sodium chloride, CDTA (trans-1,2-cyclohexylendinitrilo tetraacetic acid) and NaOH ($pH = 5–5.5$) was added to samples and standards in order to solve these problems. WTW LF-330/SET conductometer was used for conductivity measurements and Metrohm 691 model pH meter for pH measurements.

Before performance tests with ED, limiting current measurements were carried out. 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. By doing

Table 1. Limiting voltage and limiting current density values

Solution (equivalent ratios)	Electrical conductivity (μS/cm)	Limiting voltage (V)	Limiting current density (A/m^2)
$F^- : Cl^-$ (1 : 10)	160	7.00	2
$F^- : Cl^-$ (1 : 25)	330	8.32	6
$F^- : SO_4^{2-}$ (1 : 10)	150	7.27	2
$F^- : SO_4^{2-}$ (1 : 25)	353	7.89	5
$F^- : Cl^- : SO_4^{2-}$ (1 : 10 : 10)	270	7.00	5
$F^- : Cl^- : SO_4^{2-}$ (1 : 25 : 25)	453	7.95	7

it this way, the solution concentration in the feed could be maintained constant at a desired level during the experiments. If the applied current changed, the obtained potential values will change linearly until a limiting current point has been reached. After this point, there is a sharp change in slope. This switching point was determined as limiting current point. In experimental studies, 80% of the limiting voltage was applied in constant-voltage mode operation. The applied voltage values and respective limiting current density values of each study are summarized in Table 1.

RESULTS AND DISCUSSION

Fluoride Removal in the Presence of Chloride Ion

The experiments were conducted with a mixture prepared at different ratios of chloride and fluoride ions, keeping the fluoride concentration in the mixture constant (2 mg F^-/L). The ratios of equivalent concentrations of ionic species in the mixture were adjusted as $F^- : Cl^-$(1 : 10) and $F^- : Cl^-$ (1 : 25) in binary mixtures. Histories of change in fluoride and chloride ion concentrations at any time over initial feed concentration (C/C_0) using different equivalent ratios of chloride are given in Figs. 1 and 2. The concentrated (C) and diluted (D) streams were monitored for fluoride and chloride ion concentrations and conductivity values versus time. Fluoride and chloride ion concentrations of dilute and concentrated stream were measured at certain time intervals until the operation time needed for reaching 0.01A. As shown in Fig. 1, in 4 minutes 35% of fluoride and 51% of chloride removed from solutions. The concentrations of fluoride and chloride ions in the resulting solution were 1.3 mg/L and 18 mg/L, respectively. As seen in Fig. 2, increasing the amount of chloride ions in the solution ($F^- : Cl^- = 1 : 25$) facilitated

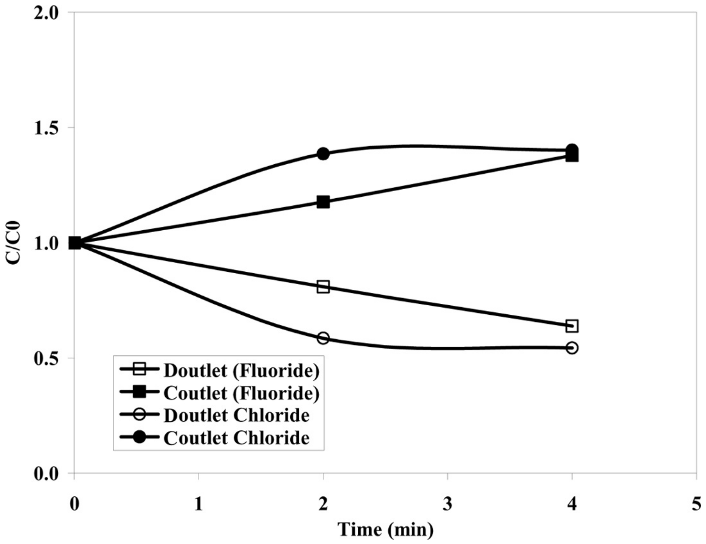

Figure 1. Concentration change of fluoride vs. time in the presence of chloride. (F^- : Cl^- = 1 : 10), applied voltage is 7.0 V, flow rate is 1.6 L/min at 25°C.

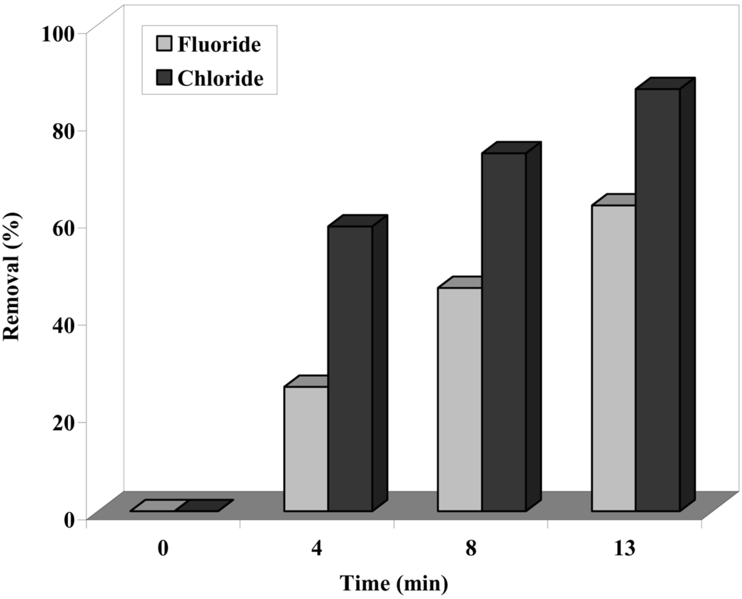

Figure 2. Percent removal of fluoride and chloride vs. time from a binary mixture. (F^- : Cl^- = 1 : 25), applied voltage is 8.32 V, flow rate is 1.6 L/min at 25°C.

the fluoride transport. After 13 min of operation time, 63% of fluoride and 87% of chloride were removed from the solution. The concentrations of fluoride and chloride ions in the resulting solution were 0.7 mg/L and 12 mg/L, respectively.

Fluoride Removal in the Presence of Sulfate

The experiments were conducted with a mixture prepared at different ratios of sulfate and fluoride ions, keeping the fluoride concentration in the mixture constant (2 mg/L).

The ratios of equivalent concentrations of ionic species in the mixture were adjusted as $F^- : SO_4^{2-}$ (1 : 10) and $F : SO_4^{2-}$ (1 : 25) in binary mixtures. Effect of sulfate concentration on separation of fluoride was shown in Figs. 3 and 4. For the case of mixture containing $F^- : SO_4^{2-}$ (1 : 10), percent removal of fluoride was 48% (it was 35% in the presence of chloride for the mixture of $F^- : Cl^-$ (1 : 10)) and only 33% of sulfate removed from solutions. The concentrations of fluoride and sulfate ions in the treated solution were 1.0 mg/L and 33.6 mg/L, respectively. As can be seen in Fig. 4, when the amount of sulfate in the mixture was increased ($F^- : SO_4^{2-}$ (1 : 25)), operation time increased. After 16 min of operation, 93% of fluoride and 51% of sulfate were removed from the solution.

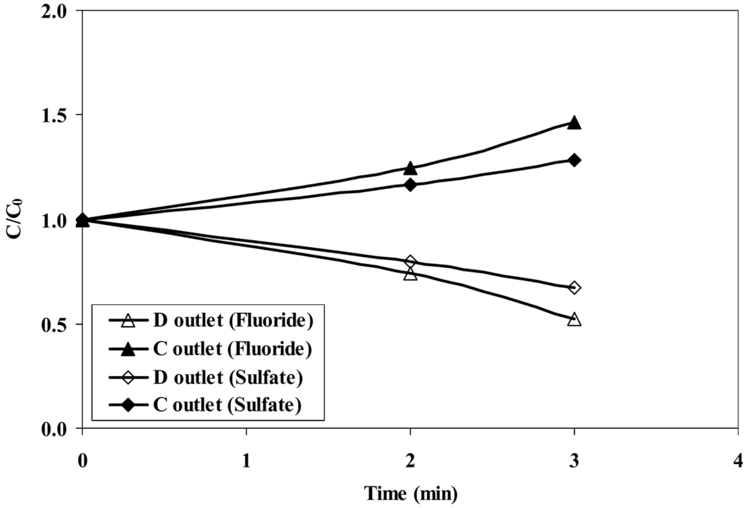

Figure 3. Concentration change of Fluoride vs. time in the presence of sulfate. ($F^- : SO_4^{2-} = 1 : 10$), applied voltage is 7.27 V, flow rate is 1.6 L/min at 25°C.

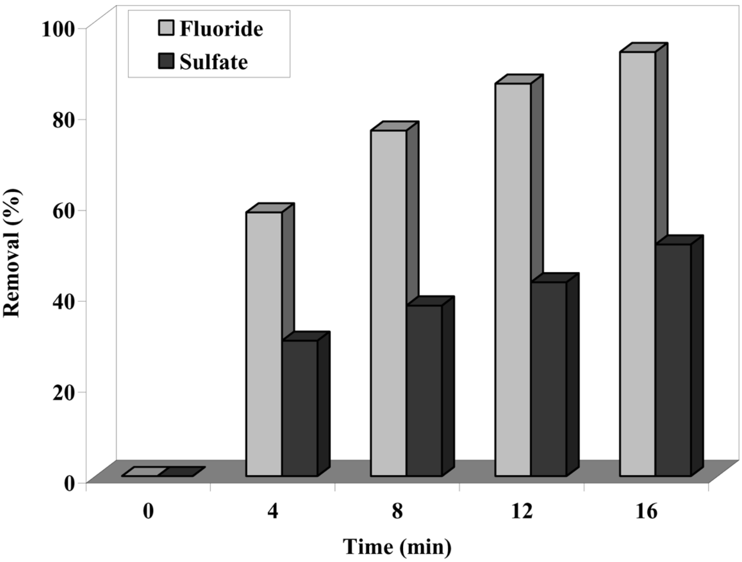

Figure 4. Percent removal of fluoride and sulfate vs. time from a binary mixture. ($F^- : SO_4^{2-} = 1 : 25$), applied voltage is 7.89 V, flow rate is 1.6 L/min at 25°C.

The concentrations of fluoride and sulfate ions in the treated solution were 0.13 mg/L and 61.8 mg/L, respectively.

Removal of Fluoride from a Ternary Solution Containing both Chloride and Sulfate

The experiments were conducted with a mixture at a combination of $F^- : Cl^- : SO_4^{2-}$ (1 : 10 : 10). Percent removal of fluoride, chloride, and sulfate were 64, 90, and 46%, repectively, in 9 min (Fig. 5). The concentrations of fluoride, chloride, and sulfate ions in the treated solution were 0.7 mg/L, 3.8 mg/L, and 27.0 mg SO_4^{2-}/L, respectively. When the equivalent amounts of chloride and sulfate in the mixture were increased ($F^- : Cl^-: SO_4^{2-} = 1 : 25 : 25$), operation time became longer and percent removal of fluoride, chloride, and sulfate increased. The increased ionic strength of the solution facilitated transport of each species. After 20 min, the percent removal of fluoride, chloride and sulfate were 96%, 98%, and 53%, respectively (Fig. 6). The concentrations of fluoride, chloride, and sulfate ions in the treated solution were 0.08 mg/L, 1.7 mg/L, and 59 mg/L, respectively.

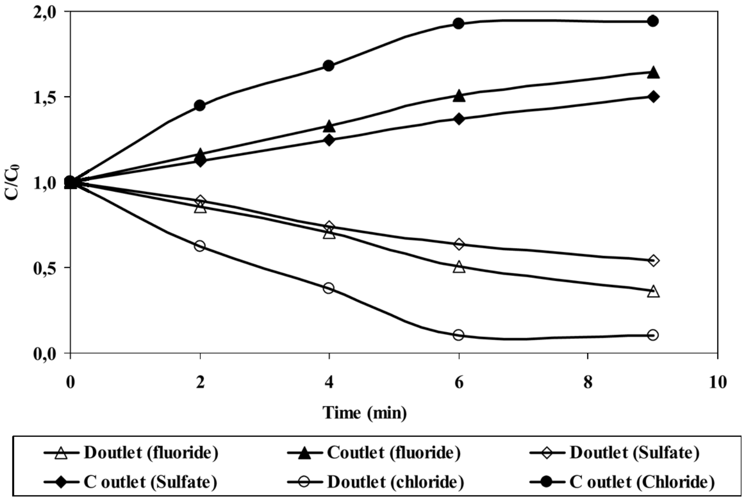

Figure 5. Concentration change of fluoride vs. time in the presence of chloride and sulfate ($F^- : SO_4^{2-} : Cl^- = 1 : 10 : 10$), applied voltage is 7.0 V, flow rate is 1.6 L/min at 25°C.

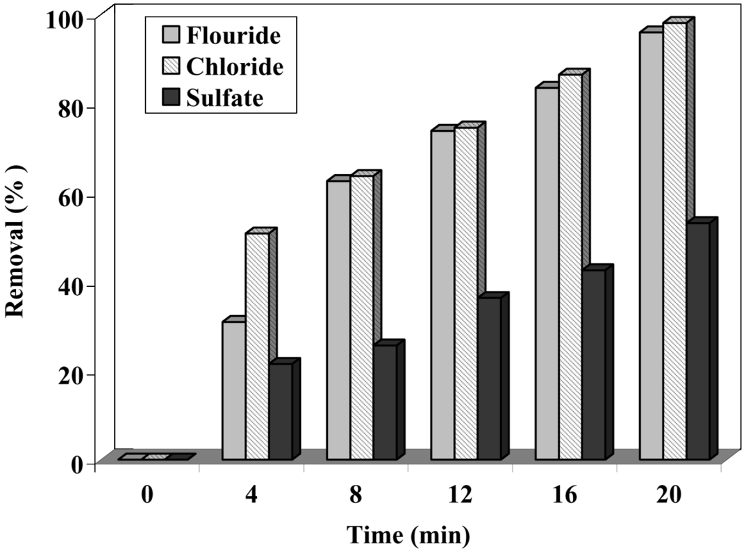

Figure 6. Percent removal of fluoride, chloride and sulfate vs. time from a ternary mixture. ($F^- : SO_4^{2-} : Cl^- = 1 : 25 : 25$), applied voltage is 7.27 V, flow rate is 1.6 L/min at 25°C.

Table 2. Effect of ionic species on the SPC

Solution (equivalent ratios)	SPC (Wh/L)
$F^- : Cl^-$ (1 : 10)	0.0082
$F^- : Cl^-$ (1 : 25)	0.0652
$F^- : SO_4^{2-}$ (1 : 10)	0.0085
$F^- : SO_4^{2-}$ (1 : 25)	0.0500
$F^- : SO_4^{2-} : Cl^-$ (1 : 10 : 10)	0.0303
$F^- : SO_4^{2-} : Cl^-$ (1 : 25 : 25)	0.0768

As seen from Figs. 5 and 6, percent removals of monovalent anions (fluoride and chloride) were higher than sulfate ion in the range of studied concentrations of these ions. 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 they are considered to be transported more slowly because of increasing hydrated radius of ions and ionic charges. The effect of ionic size could be explained in a way that the larger the ion, the more its transport through the membrane is sterically hindered. When the hydrated radius of ions were compared, it was seen that the order of hydrated radius is $Cl^- < F^- < SO_4^{2-}$ (Table 3) (20). Here, this was observed especially with sulfate containing salts due to the attraction of monovalent cations by sulfate ions in the salt solution and the retardation of these cations for their transport through the membranes.

Specific Power Consumptions

Specific power consumption can be described as the energy needed to treat unit volume of solution. The effects of co-existing ions on specific power consumption (SPC) were studied. SPC was calculated using the following equation:

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

Table 3. Hydrated radii of ions

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

Where U is the applied potential (V), I the current (A), V_D the dilute stream volume (L), t time (min). The calculated specific power consumption (SPC) values can be seen in Table 2. As summarized in Table 2, SPC values increased as the conductivity of the solution increased.

CONCLUSIONS

Removal of fluoride from water containing low concentration of fluroide (2 mg F^-/L) has been carried out using ED process. The results of this study show that electrodialysis is capable of being used to remove low concentration of fluoride from water in the presence of co-existing ions such as chloride and sulfate. When the equivalent ratios of chloride and sulfate ions in the mixture increased, the concentration of fluoride in the treated solution decreased below the permissible level for drinking water. With the solution containing both fluroide and chloride ($F^- : Cl^- = 1 : 25$), the concentrations of fluoride and chloride ions remained in the solution were 0.7 mg/L and 12 mg/L after ED process, respectively. The remaining values were 0.13 mg F^-/L and 61.8 mg SO_4^{2-}/L for the solution containing both fluoride and sulfate ions ($F^- : SO_4^{2-} = 1 : 25$).

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