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Removal of Fluoride from Geothermal Water by Electrodialysis (ED)

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Abstract: Removal of fluoride from geothermal water by electrodialysis (ED) was studied. ED operation was performed according to two methods. In the first method, before the ED operation, the pH of geothermal waters was adjusted to 7–7.5 by the addition of the HCl solution to prevent the precipitation of divalent salts in the concentrate compartment. In the second method, geothermal water was pretreated to precipitate the calcium ions. It was obtained that fluoride was effectively removed from geothermal water by electrodialysis using both of these pretreatment methods. However, it is preferable to use the first method because of its technically simple procedure and lower cost of chemicals used.

Keywords: Electrodialysis, fluoride, geothermal water, water treatment

INTRODUCTION

The element fluorine as fluoride is present in waters, minerals, most foods, and animal tissues. Surface waters generally do not contain more than 0.3 mg/L of fluoride unless they are polluted from external sources (1). The optimum fluoride level in drinking water for general good health set by World Health Organization (WHO) is considered to be between 0.5 and 1.0 mg/L (2). USA EPA established a discharge

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standard of 4 mg/L for fluoride from wastewater treatment plants. High concentrations of fluoride, in drinking water result in dental, skeletal fluorosis, and several neurological damages (3–6).

Many methods such as adsorption, chemical precipitation, ion exchange, and membrane processes (RO, ED) have been developed to remove excess fluoride 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 the regeneration step (7–11).

Electrodialysis (ED) is a membrane process in which ions are transported through ion permeable membranes from one solution to another under the influence of an applied electrical potential (12,13). In a typical ED cell, a series of anion and cation exchange membranes are arranged in an alternating pattern between an anode and a cathode to form individual cells. When a DC power is applied between two electrodes, the cations move to the cathode and anions to the anode passing through negatively charged cation exchange and positively charged anion exchange membranes, respectively. Thus, ion concentrations increase in alternate compartments with a simultaneous decrease of ions in other compartments (14–18).

Banasiak et al. performed a study to remove fluoride from ground water by ED and determined the influence of applied voltage and initial salt concentration of a solution (19). It was observed that desired drinking water can be obtained by ED of ground water with fluoride and nitrate concentrations above Drinking Water Guidelines levels. But membrane fouling during ED is a major limiting factor in its use for water treatment (19).

In another study, the effect of applied voltage, feed flow rate, fluoride concentration in the solution, and the effect of the other anions as sulfate, chloride were investigated as experimental parameters on fluoride removal from aqueous solution by ED (20).

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 the ACS membrane because of its best fluoride rejection and poor sulfate rejection (21).

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 (22).

Some studies were performed to reduce fluoride by ED from brackish water and it was demonstrated that ED is a reasonable process for removing fluoride from brackish water (7,22). Due to the 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. Because of 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. In the second method, the brackish water was treated with some chemicals before ED operation to prevent the precipitation of the calcium ions (7,22).

The aim of this study is to remove fluoride from Balcova geothermal water containing 1026 mg/L of TDS and 7.72 mg/L of fluoride by electrodialysis and to select the most efficient and suitable pretreatment method for F^- removal.

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 (each 1L) were used for holding the diluted, the concentrated, and the electrode rinse solutions. The electrodes are platinum plated (anode) and stainless steel (cathode) (23).

All reagents were of analytical grade and high quality ultra pure water was used for preparing all solutions. Fluoride solutions were prepared from NaF standard solutions (WTW standard fluoride solution, 10.0 g F^-/L).

The geothermal water was obtained from Balçova geothermal power plant region, Izmir, Turkey. Composition of the geothermal water was shown in Table 1. All water samples were stored in clean fluoride-free plastic bottles.

The analysis of fluoride, chloride, and sulfate ions were performed by Shimadzu model ion chromatography equipment (Model LC 10 A*i*). Also, an ion selective eletrode system F-ISE (WTW F800 Fluoride Combination Electrode) connected to the WTW inoLab pH/ION 735 ionmeter was used for fluoride measurements.

Table 1. Characteristics of the geothermal water

Ionic species	Concentration (mg/L)	Ionic species	Concentration (mg/L)
*Na^+	353.50	■Cl^-	208.96
*K^+	26.55	■SO_4^{2-}	176.56
*Ca^{2+}	28.17	◆F^-	7.72
*Mg^{2+}	2.14	NO_3^-	•N.M.
▲B (mg/L)		8.5–9.5	
TDS (mg/L)		1026	
Salinity		0.9	
pH = 8.42		EC = 1651 μS/cm	

*AAS; ◆ISE; ■IC; ▲Spectrophotometric; •N.M.: Not measured.

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 this problem.

A WTW LF-330/SET conductometer was used for conductivity measurements and Metrohm 691 model pH meter for pH measurements. Na^+, K^+, Mg^{2+}, Ca^{2+} ions concentrations have been determined by Varian 10 Plus Model Atomic Absorption Spectrophotometer.

In our studies, the fluoride separation tests were carried out with Balçova geothermal water containing 7.72 mg F^-/L and applying 2.7×10^{-3} m/s as linear flow rate at room temperature. Limiting current measurement was carried out before the performance test. The concentrated (C) and diluted (D) streams were monitored for concentration of anions (fluoride, chloride, and sulfate), pH, current, and conductivity values by time. The measured data were converted to their dimensionless forms by dividing them to their initial values. The ED operation was carried out according to two methods; with only pH adjustment and after a chemical pretreatment of Balçova geothermal water to precipitate calcium ions.

In the first method, to minimize the precipitation risk before electrodialysis operation, the pH of the Balçova geothermal water was adjusted to 7.0–7.5 by the addition of concentrated HCl solution. Separation tests were carried out applying 10.02 V as voltage and 2.7×10^{-3} m/s as linear flow rate at room temperature.

In the second method, before ED operation, a chemical pretreatment of Balçova geothermal water was carried out to precipitate the calcium ions. This was achieved by the successive addition of 1.0 mmol Na_2CO_3 and 1.5 mmol NaOH into 1 L of Balçova geothermal water. After one day of waiting for settling, the water was filtered through filter paper and pH of the geothermal water was adjusted to 7.0–7.5 by addition of 12 M HCl. The ED operation was carried out with the pretreated water at 10.63 V as voltage (LC) and with a linear flow rate of 2.7×10^{-3} m/s.

RESULTS AND DISCUSSION

Fluoride Removal by ED After Only pH Adjustment of Geothermal Water

In this method, before electrodialysis operation pH of the Balçova geothermal water was adjusted to 7.0–7.5 by addition of concentrated HCl solution.

For each run of the experiment, concentrated, diluted, and electrode rinse reservoirs were filled with 1 L of feed solution. The ED operation was carried out applying 10.02 V as voltage and 2.7×10^{-3} m/s as linear flow rate at room temperature. Figure 1 shows the changes in fluoride concentration, current, and conductivity values during electrodialysis experiment by

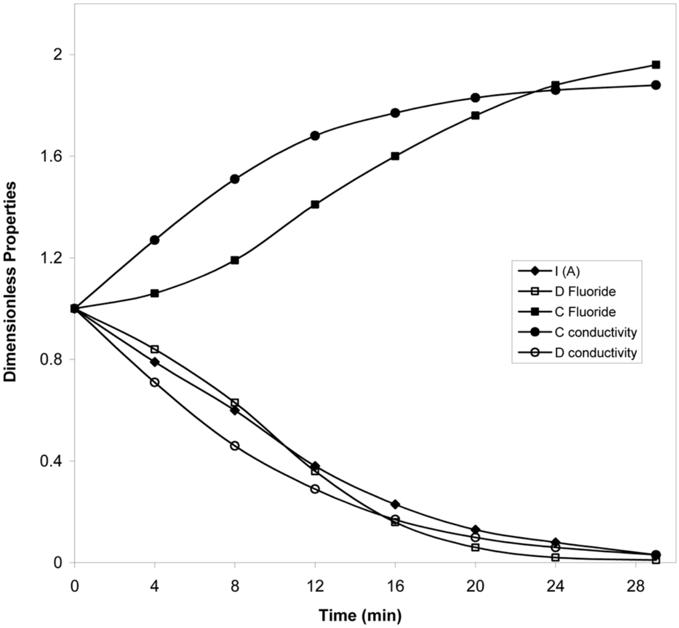

Figure 1. Dimensionless properties vs. time graph for Balçova geothermal water (pH was adjusted by HCl to 7.0 before ED) C: Concentrated, D: Diluted compartments, Voltage applied: 10.02 V, Linear feed flow rate: 2.7×10^{-3}m/s.

time in which fluoride concentrations were determined by ion selective electrode method. The characteristics of geothermal water before and after 29 minutes of electrodialysis operation were given in Table 2.

Variations of fluoride, chloride, and sulfate ion contents in diluted and concentrated compartments versus time during electrodialysis experiment were shown in Fig. 2. It was obtained that the competition between fluoride and chloride ions was certain. However, the removal rate of fluoride ions was more than that of sulfate ions. In the first 8 minutes, mainly chloride ions were removed. After the eighth minute of the experiment, the slope of the fluoride curve increased. On the other hand, after about 80–90% of fluoride and chloride ions were removed, the slope of the sulfate ion curve increased.

Table 4 shows the percent removal for fluoride, chloride, and sulfate ions during electrodialysis experiment. As seen here, the percent removal of monovalent anions (fluoride and chloride) was higher than divalent ions like 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 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

Table 2. Characteristics of the Balçova geothermal water* before and after ED**

	Concentration (mg/L)	
Ionic species	Before ED	After ED
Na^+	353.00	15.10
K^+	26.50	0.70
Ca^{2+}	28.10	0.21
Mg^{2+}	2.13	0.10
Cl^-	211.50	0.50
SO_4^{2-}	176.55	17.04
F^-	7.72	0.06
NO_3^-	•N.M.	•N.M.
B	9.20	8.30
TDS (mg/L)	1026	33
Salinity	0.9	0.0
pH	7.01	6.05
EC (μS/cm)	2140	73

•N.M.: Not measured.

*pH was adjusted to 7.0 by addition of HCl before ED.

**Voltage applied: 10.02 V.

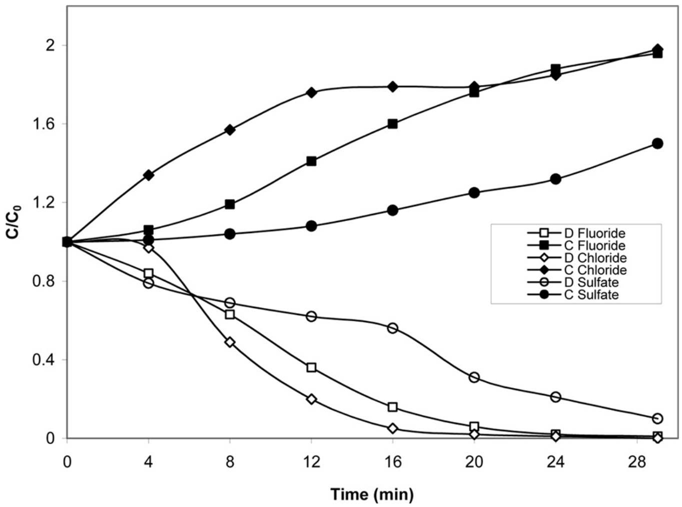

Figure 2. Variations of fluoride sulfate and chloride contents vs. time graph for Balçova geothermal water (pH was adjusted to 7.0 before ED) C: Concentrated, D: Diluted compartments, Voltage applied: 10.02 V, Linear feed flow rate: 2.7×10^{-3} m/s.

Table 3. Characteristics of the pretreated Balçova geothermal water by precipitation followed by pH adjustment before and after ED*

	Concentration (mg/L)	
Ionic species	Before ED	After ED
Na^+	259.01	10.06
K^+	26.44	0.54
Ca^{2+}	5.42	0.03
Mg^{2+}	1.85	0.01
Cl^-	307.95	0.98
SO_4^{2-}	157.01	18.68
F^-	7.72	0.07
NO_3^-	•N.M.	•N.M.
B	8.40	7.60
TDS (mg/L)	956	32
Salinity	0.9	0.0
pH	7.09	6.15
EC (µS/cm)	2010	66

•N.M.: Not measured.

*Voltage applied: 10.63 V.

Table 4. Removal of anions (F^-, Cl^-, SO_4^{2-}) from pH adjusted and pretreated Balçova geothermal water

	pH adjusted Balçova geothermal water			Pretreated Balçova geothermal water		
Time (min)	F^- Removal (%)	Cl^- Removal (%)	SO_4^{2-} Removal (%)	F^- Removal (%)	Cl^- Removal (%)	SO_4^{2-} Removal (%)
4	15.78	2.53	20.99	21.35	46.25	25.39
8	37.13	50.68	30.78	48.77	80.85	36.17
12	64.17	80.47	37.70	74.39	95.20	46.87
16	83.57	94.69	44.47	90.43	98.12	59.62
20	93.79	98.01	68.54	97.02	99.45	73.41
24	97.80	99.49	79.12	99.09*	99.68*	88.07*
29	99.22	99.76	90.35	•N.M.	•N.M.	•N.M.

•N.M.: Not measured.
*Data for 25th minute.

sterically hindered. When the hydrated radius of ions were compared, it was seen that the order of the hydrated radius is $Cl^- < F^- < SO_4^{2-}$. 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 (15). At the end of the experiment, 99% of removal for fluoride, about 100% of removal for chloride, and 90% of removal for sulfate were obtained.

As a result, fluoride ions could be removed easily from Balçova geothermal water by ED. For Balçova geothermal water after pH adjustment, fluoride concentration was found to be below 1.00 mg/L after 18 minutes of electrodialysis experiment. At the end of the experiment after 29 minutes, the remaining fluoride concentration was found as 0.06 mg/L. The results of fluoride analysis with fluoride selective electrode and ion chromatography agreed well with each other.

Fluoride Removal by ED after Precipitation of Calcium Ions followed by pH Adjustment of Geothermal Water

In this second method, before ED operation, a chemical pretreatment of Balçova geothermal water was carried out to precipitate the calcium ions followed by a pH adjustment. The characteristics of pretreated Balçova geothermal water before and after 24 minutes of electrodialysis operation were given in Table 3. Changes in fluoride concentration, current and conductivity values during electrodialysis experiment by time were shown in Fig. 3.

Variations of fluoride, chloride, and sulfate ions by time during electrodialysis experiment were shown in Fig. 4. After eight minutes of the electrodialysis experiment, the removal rate of sulfate ions increased as observed in the previous method. The removal rates of fluoride and chloride ions were larger than that of sulfate ion.

The percent removal for fluoride, chloride, and sulfate ions during electrodialysis experiment were shown in Table 4. At the end of the experiment, 99% of the removal for fluoride, about 100% of the removal for chloride, and 88% of the removal for sulfate were obtained.

For pretreated Balçova geothermal water, fluoride concentration was found to be below 1 mg/L after 14 minutes of electrodialysis experiment. At the end of the experiment after 25 minutes, fluoride concentration was found as 0.06 mg/L.

Electrodialysis experiments for pretreated Balçova geothermal water and for Balçova geothermal water after only pH adjustment were completed in 25 and 29 min, respectively. Difference in the time of

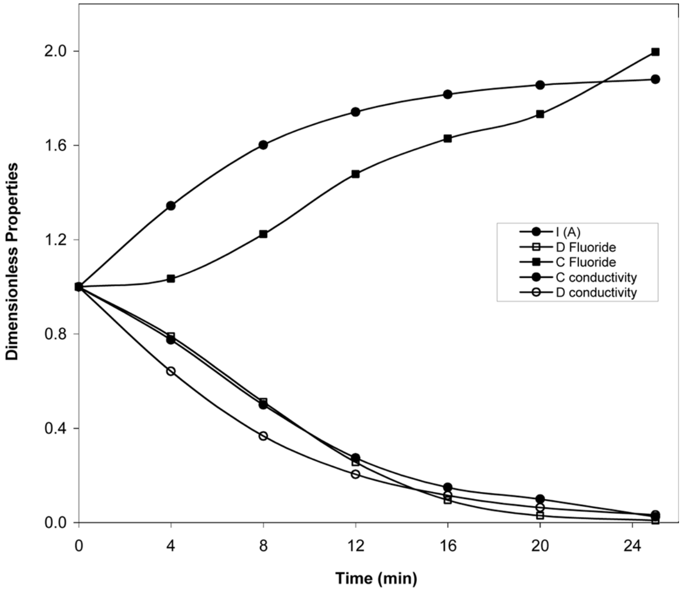

Figure 3. Dimensionless properties vs. time graph for Balçova geothermal water (after precipitation followed by pH adjustment) C: Concentrated, D: Diluted compartments, Voltage applied: 10.06 V, Linear feed flow rate: 2.7×10^{-3} m/s.

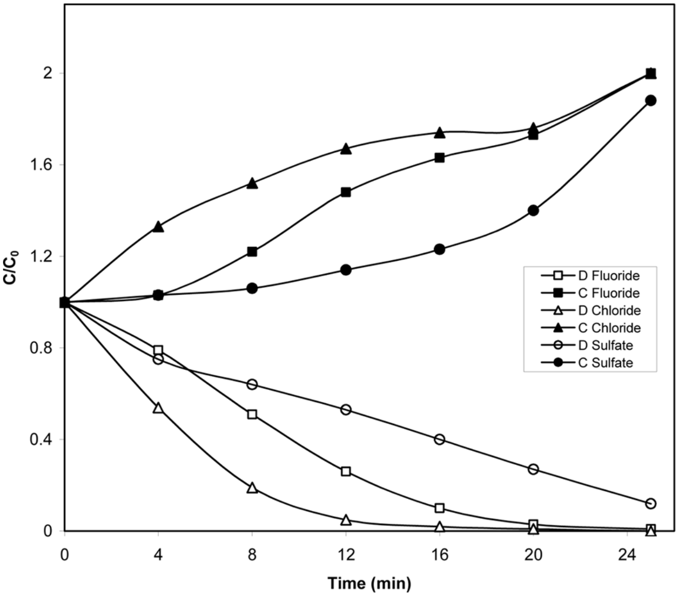

Figure 4. Variations of fluoride chloride and sulfate contents vs. time graph for Balçova geothermal water (after precipitation followed by pH adjustment) C: Concentrated, D: Diluted compartments, Voltage applied: 10.06 V, Linear feed flow rate: 2.7×10^{-3} m/s.

electrodialysis experiments can be considered to be due to some difference in applied potential values and the number of ionic species in the solutions.

The efficiencies of each run were evaluated as specific power consumption with the electrical energy consumed only in stack. Specific power consumption for each set of potential and flow rate was calculated as follows.

$$SPC = \frac{U \int_0^1 I(t)dt}{V_D}$$

where E 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 were 0.71 for pH adjusted Balçova geothermal water and 0.56 for pretreated Balçova geothermal water with precipitation followed by pH adjustment. According to the result obtained, one could conclude that the difference in specific power consumption values is due to the difference in applied potential values and the number of ionic species in the solution.

Cost analyses have been carried out for both methods as a function of chemicals employed during the pretreatments. The prices for treatment of 1 m^3 of only pH adjusted and chemically pretreated Balçova geothermal water with precipitation followed by pH adjustment were calculated as 0.72 €/m^3 and 4.43 €/m^3, respectively based on the prices of chemicals given in Merck catalog (2008–2011).

CONCLUSIONS

Removal of fluoride from Balçova geothermal water containing 7.72 mg F^-/L has been carried out using ED process. To avoid the risk of precipitation of bivalent salts in the concentrated compartment, the ED operation was carried out according to two methods; with only pH adjustment of geothermal water and with a chemical pretreatment of Balçova geothermal water to precipitate calcium ions. The ED experiments for pretreated Balçova geothermal water by precipitation followed by pH adjustment and for only pH adjusted Balçova geothermal water were completed after 25 and 29 minutes, respectively. Fluoride was effectively removed from Balçova geothermal water by ED applying both methods. At each methods, we obtained approximately 99% of removal for fluoride at the end of the ED experiments. The product water at the end of ED process meets the requirements of drinking water for fluoride. However, it is preferable to use the ED process with only the pH adjustment method because of its simple procedure and lower cost of chemicals used. In the second method, some additional chemicals were added during the pretreatment step and this may be another disadvantage for environmental impact.

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