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Research Article

Economic evaluation of fluoride removal by membrane capacitive deionization

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ABSTRACT

Today, one of the most important issues of all is the supply of drinking and utility water, which is the most basic need for human beings, to be healthy and reliable, economical. Some substances in natural water sources pose a danger to living creatures when they exceed certain concentrations. Fluoride, which can be commonly found in water as a result of natural or industrial effects, poses various risks for the living not only in its deficiency, but also its excess. Therefore, the fluoride concentration should be under control. Membrane Capacitive Deionization Process is an effective method to remove ions from water. In this study, firstly, optimum conditions have been determined by working on the removal of fluoride from groundwater with MCDI which is prepared synthetically. Subsequently, the groundwater, which was obtained from Isparta province and containing 7.71 mg/L fluoride, was treated by the membrane capacitive deionization method at the optimum conditions determined by 99%. Groundwater fluoride concentration has been reduced below the drinking water fluoride limit. For this treatment, 0.06 kWh/m^3 energy was expensed and this corresponds to an energy cost of $ 0.006/m^3. These results are quite economical when compared to other groundwater fluoride removal methods.

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INTRODUCTION

Water is one of the most basic needs for the existence and health of living creatures, and a healthy and safe water supply becomes very important in the supply of water as drinking water and utility water. Increasing living standards together with socio-economic developments boosts per capita drinking and utility water requirements as well. The increase in daily water consumption as a result of population growth, rural-urban migration, and urbanization, and industrialization necessitates the supply of drinking water from surface and groundwater resources. Although all water contain anions such as chlorides and sulfates, in particular, this type of anions and cations do not pose a significant risk unless their total salt concentration exceeds the acceptable limit [1]. However, anions such as fluoride and nitrate can cause health problems. Fluoride (F^-) contamination commonly occurs in the groundwater and the highest F^- concentration reported in groundwater of South Asia, Africa and the Middle East countries [1, 2].

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Table 1. Operating costs of different treatment methods in fluoride removal

Treatment technigues	F- concentration (mg/L)	Removal efficiency (%)	Operation cost (cost/m^3)	Reference
Electrochemical Treatment Iron electrode	25	40	0.059 $	[6]
Electrocoagulation Al electrode and NaCl conducting agent	1.49–7.89	94 – 91.6	0.027–0.14 $	[7]
Electrocoagulation	8.63	84.8	0.531 €	[8]

The presence of F^- in drinking water has both beneficial and harmful effects on the health of living creatures, depending on the limit values of concentration of F^-. F^- at a range of 0.5 to 1.0 mg/L has positive effects on teeth and bones. However, F^- concentrations greater than 1.5 mg/L cause permanent bone and joint deformities, dental and skeletal fluorosis for children, in particular. When exposed to a F^- concentration greater than 4 mg/L, on the other hand, neurological damages and further toxic effects may occur. It is observed that in some countries around the world such as China, India, Kenya, Mexico, Thailand, and especially in Isparta province in Turkey, the concentration of F^- ions in groundwater used for drinking water exceeds acceptable drinking water standards. Studies conducted in Isparta suggested that volcanic lake sediments, possible sources of F^-, are over 20 km^2 and may reach up to 60 m in thickness in the region, that the fluoride content in trachyandesites and tuffites in Isparta-Gölcük region increased parallel to the abundance of biotite, and that this could result in F^- enrichment in groundwater. It was revealed that these groundwater caused dental fluorosis, which was known as Isparta Brown Stain in the 1960s and the use of groundwater as a water source was stopped in the mid-1990s [3].

Various techniques such as adsorption, ion exchange, reverse osmosis, and electrodialysis are still broadly utilized for fluoride removal from the water today [1, 4, 5]. All of these techniques have some disadvantages such as impracticality, low efficiency, and high operating costs.

Some parameters such as inlet concentration, removal efficiency and cost in fluoride removal with different treatment techniques are given in Table 1.

In recent years, the use of capacitive deionization (CDI), which is defined as a practical, low cost and eco-friendly electrochemical desalination process, becomes popular. In CDI, the electrode compartments directly participate in the ion removal/concentration process, with oxidation/reduction at the electrodes; electrons are transferred by electrostatic adsorption/ desorption. In the CDI process, electrical double layers are formed on the anode and cathode surfaces created by the applied voltage and thus, oppositely charged ions are effectively captured at the opposite electrodes. Membrane capacitive deionization (MCDI), on the other hand, is a technology that increases the efficiency of CDI created by adding ion-selective membranes to the surfaces of CDI electrodes [9].

Table 2. Ranges of MCDI operating parameters

Parameter	Range
Current (A)	0 – 60
Voltage (V)	0 – 2
Inlet Flow (L/min)	0 – 2
Time (sec.)	unlimited
Conductivity (mS/cm)	0 – 30.000

In this study, the purification of F^- of different concentrations from synthetic groundwater through the MCDI process by using the optimum conditions obtained in previous studies with MCDI technology was investigated. Subsequently, fluoride-containing groundwater supplied from Isparta was purified and the costs were worked out [10].

MATERIALS AND METHODS

MCDI Process and Operation Conditions

Figure 1 shows the schematic representation of the Voltea Brand MCDI reactor, which was used in the study.

The MCDI system consists of 24 cells made of PVC. Each cell contained a graphite current distributor (thickness δ=250 μm), chemically identical porous carbon electrodes to work as cathode and anode (δe=362 μm), anion- and cation-selective membranes to control ion flow (Neosepta AM-1 and Neosepta CM-1, Tokuyama Co., Japan, δ≈130 μm) and textile separator (δ=115 μm) that allowed water flow and separated the electrodes from each other. The resistance of the carbon electrodes was 1 (±0,2) Ω·cm^2, and the total electrode area was 2.7 m^2. The anion- and cation-selective membranes had resistance values of approximately 2Ω cm^2. Table 2 shows the operating ranges of the different parameters used in the device.

The MCDI device could be operated automatically or manually at three stages: "purification", "preliminary" and "concentrated flow". In automatic mode, optimum flow is cal-

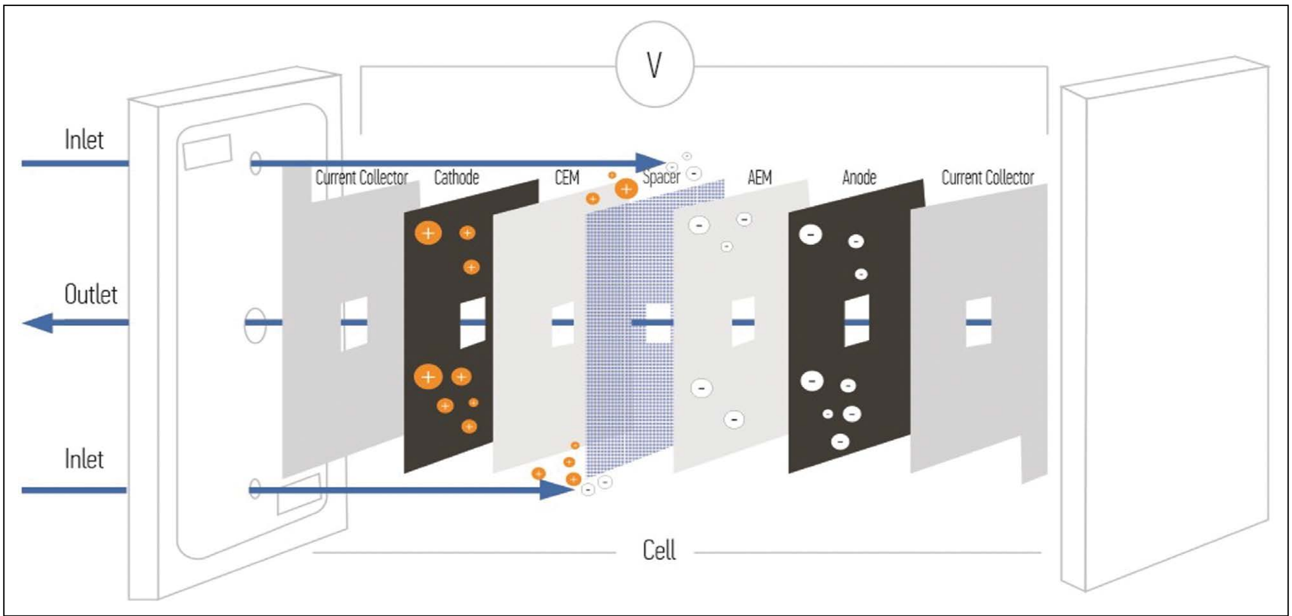

Figure 1. Schematic representation of MCDI process [11].

culated after entering data such as conductivity, flow rate, voltage, desired removal efficiency, treatment time, and desorption time, etc. on the calculation monitor.

Automatic mode starts with the concentrated flow stage, which refers to fully discharge the electrodes in order to run them in full capacity. At this stage, the water to be purified is taken into the reactor and electrode potentials (negative to positive) are prepared for adsorption. Afterward, preliminary stage starts. At this stage, the concentrated flow in the reactor is fully taken out of the reactor. Finally, the adsorption process begins. In previous experiments conducted with this device, optimum conditions were determined to be 24 min for adsorption, 1 min for system preparation, 1.5V for maximum potential and 0.3L/min for flow rate [10, 11].

Chemical Analyses

F^- ions measurements were performed using Intellical F^- ISE Standard Electrode, which has a range of measurement between 0.01 mg/L–19 g/L. Argentometric method used for Cl^- analysis. Turbidimetric method was used for sulfate analysis, allowing analysis at a concentration of 1–40 mg/L SO_4^{2-}. The EDTA titrimetric method and related calculations were used for the Mg^{2+} and Ca^{2+} analyses [12].

Cost Analysis

In experiments made with MCDI, energy consumption was figured out using the potential and flow consumed during the adsorption and desorption stages and the costs obtained include only energy costs. Equation (1) is used only in calculating the energy consumption based on adsorption. In this equation, V1 refers to average voltage for adsorption, while A1 to average flow for adsorption, and Q to flow rate. The values used in equation (1) and (2) are average values [11].

$$Energy\ Demand\ for\ Adsorption = \left(\frac{kWh}{m^3}\right) = \frac{V_1\ x\ A_1}{Q} \quad (1)$$

To calculate the energy consumed in the adsorption and desorption stages, equation (2) was used, where a represents water recovery rate; b, concentrated flow rate; V2, average voltage for desorption; and A2, average flow for desorption.

$$Energy\ Demand\ for\ Ads.\&\ Des. = \left(\frac{kWh}{m^3}\right) = \left(a\ x\ \frac{V_1\ x\ A_1}{Q}\right) + \left(b\ x\frac{V_2\ x\ A_2}{Q}\right) \quad (2)$$

While converting energy consumption into fiscal cost, electricity unit price (71,12 krş/kW in TL or 0,116 $/kW in US Dollars), which is determined by the Turkish Electricity Distribution Corporation, was used.

Synthetic Groundwater

Studies for fluoride removal from groundwater were carried out by adding F^- at different concentrations to synthetically prepared groundwater. Generally, synthetic water are prepared on the basis of present groundwater in the region where the study is conducted. However, altered water regimes over time, meteorological conditions, and differences in underground rock/soil structures may significantly affect the content of groundwater. Therefore, while preparing synthetic groundwater, the studies conducted in Turkey and in the world were examined and the principles used in the preparation of synthetic groundwater in these studies were taken into account. Table 3 shows the content of synthetic groundwater prepared in some studies.

In the studies conducted in the world and in Turkey, especially F^--containing synthetic groundwater and real groundwater were examined [16]. Based on these studies, synthetic samples with the features given in Table 4 were prepared and F^- fluoride at different concentrations were added.

Table 3. Synthetic groundwater contents prepared in some different studies

Groundwater contents	Concentration (mg/L) [13]	Concentration mg/L) [14]	Concentration (mg/L) [15]
F^-	3.25	4.5 – 6.85	0
Cl^-	1083	10 - 150	154
SO_4^{2-}	215	0.1 - 1	319
NO_3^-	25		25
HCO_3^-	171	200 - 650	-
Na^+	448		117
Ca^{2+}	127	100 - 150	87
Mg^{2+}	136	20 - 30	0

RESULTS AND DISCUSSION

Treatment of Fluoride-Containing Synthetic Groundwater with MCDI and Cost Analysis

F^- ion with values ranging from 1–20 mg/L was added to synthetic groundwater prepared according to Table 5, and purification process was applied with MCDI. Data belonging to ion values obtained in analysis after purification processes were given in Table 5. Accordingly, removal efficiencies for F^- 1–20 mg/L inlet concentration were found to range from 99.9% to 99.04%, and as the concentration increases, the removal efficiency decreases relatively. However, for all concentrations, the F^- concentration was reduced to 1.5 mg/L, which is the fluoride limit value specified in the Regulation Concerning Water Intended for Human Consumption.

Table 4. Synthetically prepared groundwater content

Content	Ca^{2+}	K^+	Mg^{2+}	Na^+	Cl^-	SO_4^{2-}
Concentration (mM)	3	0.5	1.5	5	10	2
Concentration (mg/L)	120	20	37	115	354.5	192

The conductivity values of synthetic water range from 1430 µS/cm to 1580 µS/cm. Table 6 shows some parameter values used and obtained in the treatment of synthetic groundwater. Accordingly, the removal of conductivity for all solutions was found as 99%. While F^- removal efficiency decreases with increasing concentration, Cl^- removal efficiency decreases from 98% to 94% depending on increasing F^- concentration and SO_4^{2-} removal efficiency decreases from 99.9% to 94%. This can be explained by the competition of anions in migration to electrodes [8]. In the treatment of synthetic groundwater, energy consumption is in the range of 0.5–0.68 kWh/m³ and costs range between 0.06-0.08 $/m³.

Table 5. Ion values after treatment of synthetic groundwater

Inlet fluoride concentration (mg/L)	F^- mg/L	Ca^{2+} mg/L	Cl^- mg/L	K^+ mg/L	Mg^{2+} mg/L	Na^+ mg/L	SO_4^{2-} mg/L
1	<0.01	<1	8	<1	<1	<1	<1
2.5	<0.01	3	12	<1	2	<1	<1
5	<0.01	5	12	<1	3	<1	<1
7.5	<0.01	6	10	<1	2	2	3
10	0.04	5	18	<1	3	<1	3
12.5	0.079	6	18	<1	4	4	5
15	0.112	6	20	<1	4	3	5
17.5	0.164	7	21	2	5	8	12
20	0.193	7	24	2	5	10	11

Table 6. Parameters in synthetic groundwater treatment

Parameter	Unit									
Fluoride concentration		1	2.5	5	7.5	10	12.5	15	17.5	20
Inlet Conductivity	µS/cm	1430	1430	1440	1459	1520	1531	1548	1564	1584
Removal*	%	99	99	99	99	99	99	99	99	99
Inlet Flow	L/min	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Current*	A	6.71	7.52	7.1	6.75	7.14	7.63	6.84	6.75	8.03
Voltage*	V	1.34	1.30	1.38	1.39	1.34	1.39	1.44	1.48	1.52
Water Recovery	%	87	86.6	84	85.7	85	84.4	84.4	84	82
Energy Consumption	kWsa/m³	0.50	0.54	0.54	0.52	0.53	0.57	0.55	0.56	0.68
Cost	$/m³	0.06	0.06	0.06	0.06	0.06	0.07	0.06	0.06	0.08

*Avarage

Table 7. Ion Values of groundwater supplied from Isparta

Parameter	Conductivity μS/cm	F^- mg/L	Cl^- mg/L	SO_4^{2-} mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	Na^+ mg/L
Value	410	7.71	4	62.7	28.4	137	16

Table 8. Parameters in groundwater treatment

Cycle information	Unit	Groundwater
Inlet Conductivity	mS/cm	0.409
Removal	%	99
Inlet Flow	L/dk	0.3
Current	A	2.19
Voltage	V	0.48
Water Recovery	%	83.1
Energy Consumption	kWsa/m^3	0.06
Cost	\$/m^3	0.006

Table 9. Ion values after groundwater treatment

Parameter	Unit	Outlet concentration	Average removal %
Conductivity	µS/cm	5	99
F^-	mg/L	0.01	99.9
Cl^-	mg/L	<1	100
SO_4^{2-}	mg/L	<1	100
Ca^{2+}	mg/L	<1	100
Mg^{2+}	mg/L	2.16	99
Na^+	mg/L	<1	99.9

Treatment of Fluoride-Containing Groundwater with MCDI and Cost Analysis

Table 7 shows the values belonging to groundwater supplied from Isparta province that contains F^- above the limit values.

Corresponding to groundwater with 410 µS/cm conductivity, water prepared with NaCl solution at the same conductivity was treated with MCDI and the effect of ion content on performance was investigated. Table 8 indicates that there are differences between the treatment of groundwater using the MCDI process and the treatment of the solution prepared with NaCl. In the treatment of groundwater, a current of 2.18 A with a potential of 0.48 V was used and the conductivity removal efficiency was 99%. In the treatment of NaCl solution, on the other hand, 1.97 A-current was provided with 1.47 V potential and conductivity removal efficiency was obtained as 99.9%. The current used is directly related to the ion contents and the difference in the currents used corresponding the potentials arises from this situation. While a treatment cost of 0.019 \$/m^3 occurs in the treatment of NaCl solution, the treatment cost of groundwater was realized as \$ 0.006/m^3. This result shows that F^- removal from groundwater with the MCDI process is more economical than the other electrochemical methods given in Table 1.

As a result of the treatment of groundwater with the MCDI process; as seen in Table 9, drinking water was obtained by purifying the total conductivity of 410 µS/cm with a treatment efficiency of 99%. Groundwater F^- value of 7.71 mg/L was reduced below the limit values with a removal efficiency of 99.9%.

CONCLUSION

Healthy and safe water supply for the protection of human health is one of the most important issues today. Besides, increasing per capita water consumption due to various factors makes finding new water resources inevitable. However, when fluoride that can be found in groundwater exceeds limit values, this may lead to serious problems, especially in bone structures.

Traditional methods widely used today for the removal of F^- from water have disadvantages such as impracticality, low efficiency, and high operating costs. As an alternative to traditional treatment methods, the use of capacitive deionization (CDI), a practical, low-cost and eco-friendly, and highly efficient electrochemical desalination process, becomes popular.

In this study, the purification of fluoride from groundwater using MCDI technology was investigated and analyzes were made for the cost of the process. We managed to treat F^- ions (7,71 mg/L) in the groundwater we analyzed, which was far above the limit values, with a removal efficiency of 99%. The cost analysis indicated that 0.06 kWh/m^3 energy was consumed for treatment, which corresponds to 0.006 \$/m^3.

As a result, it was revealed in the study that the MCDI process can be used as an alternative technology to remove F^- ions from groundwater economically and efficiently.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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