



Research Article

FLUORIDE CONTAMINATION IN GROUNDWATER AND ITS REMOVAL BY ADSORPTION AND ELECTROCOAGULATION PROCESSES

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Received: 10.04.2019 Revised: 16.07.2019 Accepted: 27.08.2019

ABSTRACT

Endemic fluorosis cases were detected in primary school students in Sarım and Karataş villages situated in the north-west of Sanliurfa. Fluorosis is resulted from high concentrations of fluoride in groundwater and observed in some regions of Turkey having volcanic rocks and geothermal fields. Results of fluoride analyses indicated that the concentrations in groundwater samples were above the admissible limit values for potable water ($>1.5 \text{ mg L}^{-1}$). Hence, fluoride concentration in groundwater must be decreased to an optimum level that was recommended in national and international groundwater regulations. Objectives of this work are; to study the high fluoride in groundwater of arid-semiarid region and its health effects on children and to examine its removal efficiency from groundwater by electrocoagulation (EC) and adsorption processes. Adsorption processes were performed by batch method with clay minerals. The fluoride adsorption values concorded well with both Langmuir and Freundlich equations. Low value for K_f (0.14) showed low F adsorption which can be accounted by negatively charged sites on the clay mineral. EC process including the electrodes, reactor and the power source successfully removed the fluoride from groundwater sample. F removal rate was found as 99% at the end of 4.5 h. EC method on the removal of F was more successful than F adsorption on the clay.

Keywords: Fluoride, electrocoagulation, adsorption, groundwater.

1. INTRODUCTION

One of the trace elements important for human health is fluoride (F). [1]. Natural and anthropogenic activities caused fluoride pollution in waters [2]. According to the World Health Organization, the limit for the fluoride concentration permitted for potable water is 1.5 mg L^{-1} [3]. Fluoride ions higher than the permissible level in drinking water ($F > 1.5 \text{ mg L}^{-1}$) cause negative effects such as tooth and skeletal fluorosis on human health [4,5]. The fluoride concentration shows variability in the groundwater depending on the lithological, physicochemical features of the aquifer, the hydrogeological parameters (i.e. hydraulic conductivity, porosity, storativity, transmissivity), acidity- alkalinity of the soil and rocks, the temperature, the fate of other chemical constituents and the depth of the wells. Volcanic rocks, mica minerals and thermal sources also cause fluoride contamination in natural waters. Studies have shown that high fluoride

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concentration is associated with magmatic and metamorphic rocks in groundwater in different parts of the world. [6].

Fluoride is still important in preventing dental caries. However, overdose of fluoride ingestion increases the risk of dental fluorosis [7,8]. Dental fluorosis is a developmental tooth enamel disease caused by excessive intake with a high mineral concentration during the tooth development. It also results in less mineral content and more porosity in the teeth [9]. Fluoride content between 0.5 and 1.5 mg L⁻¹ is optimum value to prevent the tooth decay. Fluoride concentrations above the 1.5 mg L⁻¹ causes dental fluorosis; and waters with an excess of fluoride concentration (>4.0 mg L⁻¹) may lead to skeletal fluorosis. In addition, high fluoride concentration may cause osteoporosis and serious problems in body [4,5,10,11]. As seen in studies in some parts of Turkey, fluoride concentration of water was found high from 1.5 to 13.7 mg L⁻¹ due to the volcanic rocks and geothermal sources [12-16]. Yeşilnacar (2010) has first detected excessive fluoride in groundwater and dental fluorosis cases in two villages situated in the north-west of Sanliurfa city (Southeast of Turkey) [17,18].

There are many fluoride removal technologies today in a worldwide such as membrane processes [19], electro dialysis [20], adsorption [2,21], ion exchange [22], coagulation and electrocoagulation [23,24]. The electrocoagulation process is an electrochemical method for the treatment of contaminated water and is a water treatment technology used to remove a wide variety of contaminants [25]. EC technology develops as a promising alternative because it provides advantages that eliminate the disadvantages of conventional methods [26]. The high energy consumption, which is seen as a disadvantage of the EC process, will be eliminated by the solar energy system established with the help of PV panels for a region with high sunshine duration. The horizontal total radiation value of the Sanliurfa region is around 1845 kWh/m² [27]. Total daylight value for the province measured as 3417 hours/year. In the light of this information, many studies have reported that PV panels are more efficient and economical [28-31]. Adsorption method is the most common method used in countryside [32]. A diverse range of adsorbents was handled for fluoride removal such as clay minerals [33], bauxite [34,35], alumina [36], cement [37] and activated carbon [38]. In this study, fluoride in groundwater and its effects on human health in arid and semi-arid region was determined, and the removal of F by adsorption and EC method was compared.

2. MATERIAL AND METHODS

2.1. Study area

The location map of studied area including the situation, location and coordinates of the Sarım and Karataş villages in Sanliurfa is given in Figure 1. The drinking water of the villages within the study area was generally supplied from the wells at 100-150 meters depth which were drilled in the last 10-15 years by the government.

2.2. Methods

2.2.1. Electrocoagulation

The experimental set-up includes electrodes, reactor, magnetic stirrer and power supply. Seven Al plate electrodes (purity 99.5%) were used in the study. The distance between both electrodes was 10 millimeters. They were connected to a direct current power unit (Rigol DP832A model, 30V, 3A).

Groundwater samples were taken from Sarım village. The characteristics of the groundwater and EC reactor are given in Table 1 and 2, respectively. Fluoride removal was performed by electrocoagulation and adsorption method on the water sample.

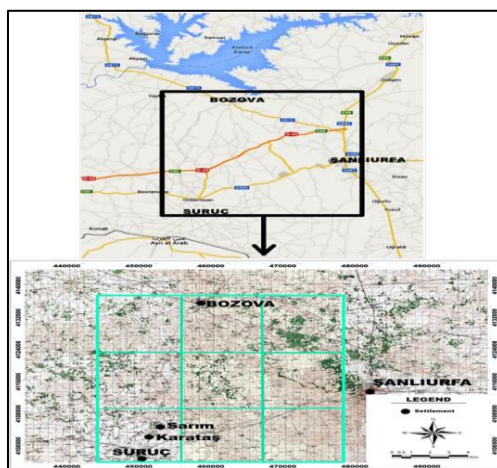


Figure 1. The location map of the studied area

Table 1. Physicochemical features of the groundwater in the studied area

Parameter	Value
pH	8.29
Electrical conductivity ($\mu\text{S}/\text{cm}$)	486
Temperature ($^{\circ}\text{C}$)	25
F^{-} (mg L^{-1})	1.65
Cl^{-} (mg L^{-1})	15.89
NO_3^{-} (mg L^{-1})	8.4
SO_4^{2-} (mg L^{-1})	14.02

In each experiment, the electrolytic reactor contained 1500 mL water. A magnetic stirrer was used at 250 rpm (IKA RH basic 2) in the EC reactor. EC tests were carried out by batch method. The oxide lamina on the Al electrode surface areas was removed by the solution of the HCl (37%) and the hexamethylenetetramine aqueous solution (3%) for 5-minute immersion before each trial. They were then assembled the reactor. The voltage and current was set to a desired value (5V-1A) through adjustment of the power supply and the experimental study was started at room temperature (25 $^{\circ}\text{C}$). The duration of the experiment was 270 min and samples were taken for 30 min intervals. The 0.45 μm syringe filters were used to filter the samples. Initial and final pH and conductivity for each sample was measured with Portable Hach-Lange HQ40d multi-measurement device. At the end of the experiment, they were cleaned with distilled water to eliminate the residuals on the electrode faces. The electrochemical reactor assembly is shown in Figure 2.

EC involves in situ generation of coagulants by electrocoagulation of aluminum electrodes. Aluminum cations are generated the anode (1) and hydrogen gas is evolved at the cathode (2). [39].



During the dissolution of Al at the anode various aqueous aluminum species are produced. The aluminum cations are transformed to polymeric species and form $\text{Al}(\text{OH})_3$ precipitate:



The fluoride removal by EC was carried out by means of a chemical substitution in which F⁻ replaced OH⁻ group from Al(OH)₃ flocs [10].



Figure 2. The set-up used in the study

Table 2. Typical features of electrocoagulation process

Electrodes	
Material	Aluminum
Shape	Rectangular plate
Size (millimeters)	90 × 200
Thickness (millimeters)	3
Number	7
Connection mode	Monopolar parallel
Effective electrode face area (cm ²)	648
Reactor	
Type	Glass
Mode	Batch mode
Dimensions (mm)	100 × 100 × 250
Volume (L)	2.5
Used water volume (L)	1.5
Stirring mechanism and rpm	Magnetic bar and 250 rpm
Power supply	
Range of Voltage (V)	0-5
Range of Current (A)	0-1

2.2.2. Adsorption

Adsorbent used in the adsorption study was clay mineral as a local material procured from Yarıntepe village, Sanliurfa. The tests were executed by Batch method. The 0.45 μm syringe filters were used to filter the samples. Fluoride analyses were carried out by Hach-Lange HQ40d

multimeter device using TISAB method [40]. Physicochemical features of the clay minerals used in adsorption tests shown in Table 3.

Table 3. Physicochemical features of the clay minerals used in adsorption tests

Clay-Yarımtepe	
Content	Concentration (%)
SiO ₂	30.506
Al ₂ O ₃	7.641
Fe ₂ O ₃	5.603
MgO	6.285
CaO	23.654
Na ₂ O	0.069
K ₂ O	2.019

The compounds of Al₂O₃ and Fe₂O₃ located in the clay minerals are thought to have increased adsorption effect.

The certain quantity of fluoride adsorbed, and percent of fluoride adsorption was calculated by means of the equation below.

$$Cs = (Co - Ce) \times V/W \quad (4)$$

And

$$\% \text{ Adsorption} = (Co - Ce) \times 100/Ce \quad (5)$$

Where Cs is the adsorption capacity (mg g⁻¹) in the solid phase at equilibrium; Co, Ce are initial and equilibrium concentrations of fluoride (mg L⁻¹), respectively. V is the volume of the aqueous phase and W is the mass (g) of adsorbent used in the experiments.

A preparatory work kinetic experiment was performed to set up the equilibration time for fluoride adsorption. Tests were made with double sampling in 50 mL polypropylene test tubes. Clay mineral samples (0.2 g) were shaken with 40 mL of fluoride solutions having 5 mg L⁻¹ of initial concentration on a reciprocating shaker with 150 rpm for 1-2-3-4-5-11-24 hours to acquire the equilibration time at room temperature and then supernatant which was filtered from syringe filtrate was poured carefully and analyzed for the residual fluoride.

Adsorption data were analyzed using linearized form of the Langmuir (Equation 6) and Freundlich isotherms (Equation 7):

$$(Ce/Cs) = (1/Qob) + (Ce/Qo) \quad (6)$$

$$\log Cs = \log Kf + 1/nf * \log Ce \quad (7)$$

where b is the Langmuir constant and Qo is the maximum amount of adsorbent that can be adsorbed. Plotting Ce/Cs versus Ce, the slope is 1/Qo and the intercept is 1/Qob. Kf and 1/nf are the empirical Freundlich constants. By plotting log Cs (amount adsorbed to adsorbent, mg g⁻¹) versus log Ce (amount of fluoride in solution, mg L⁻¹), 1/nf is calculated as the slope of the curve and the intercept is equal to log Kf [41].

3. STUDIES

3.1. Dental fluorosis cases in southeastern of Turkey

Atasoy and Yesilnacar [4] determined the high F in Sarım and Karataş groundwater and detected the dental fluorosis cases in the villages. It was reported that the dental screening was carried out by a dentist from Sanliurfa Provincial Health Directorate in a project carried out in

2010 (Figure 3) [17]. The amount of fluoride in ground water was between 1 and 4 mg L⁻¹. Sarım and Karataş samples were higher than the values reported by WHO (0.5-1.5 mg L⁻¹). High fluoride concentration in groundwater caused the dental fluorosis in the region. As a continuation of this study in order to investigate whether the problem persists, ground water samples were taken from the same wells again in 2018. According to the results of the groundwater analysis, the highest F concentration was found 2.35 mg L⁻¹ and this value was still above the permissible limit. Additionally, a female student who underwent a dental screening 10 years ago was reached and dental screening was repeated. It was found that the dental fluorosis problem was still present for the same student and the others (Figure 4) [42].



Figure 3. Some images from the dental examinations (year 2010)



Figure 4. Some images from dental fluorosis cases in 2018

3.2. Fluoride removal by electrocoagulation

The performance of EC process was estimated for the removal of fluoride from natural groundwater sample gathered from Sarım and Karataş villages in Sanliurfa. pH and conductivity of groundwater were 8.29 and 486 $\mu\text{S}/\text{cm}$, respectively. Other parameters were mentioned in Table 1. Electrocoagulation process successfully decreased the fluoride concentration below the maximum contaminant level of 1.5 mg L⁻¹ (99.4% removal). F removal rate increased with the operation time due to the arising Al⁺³ ions by aluminum anode during the process time. Table 4 showed the EC operating conditions and energy consumption. According to the results, the energy consumption increased with the decreased conductivity [43,44]. The lowest energy consumption value (0.13 kWh/m³) corresponded to the highest conductivity (469 $\mu\text{S}/\text{cm}$). In this work, the maximum energy consumption was found lower than the other F removal studies of EC [44-47]. The pH of a solution is one of the most significant parameters in EC process [48,49]. Especially in this study pH effected the removal of fluoride and performance of electrochemical process. Controlling of water pH was very difficult during the EC process due to its instability throughout

the experiment. Both of pH and conductivity were measured in certain time intervals as shown in Figure 5. Both decreased while the F removal rate was increasing. At the end of the operation time, pH and conductivity were measured as 7.7 and 291 $\mu\text{S}/\text{cm}$, respectively.

Table 4. The EC operating conditions

Parameter	EC Process
Electrode material	Al
Current density (mA cm^{-2})	1.5
Temperature ($^{\circ}\text{C}$)	25
Initial pH	8.29
Final pH	7.66
Initial electrical conductivity ($\mu\text{S cm}^{-1}$)	486
Final electrical conductivity ($\mu\text{S cm}^{-1}$)	291
Operating time (min)	270
Energy consumption (kWh m^{-3})	0.76
Energy consumption per kg fluoride (kWh kg F^{-1})	466.1

Simultaneous fluoride and ammonia from semiconductor wastewater [44], arsenic from groundwater [24], chromium (VI) from pretreated acidic semiconductor effluents [50], iron from contaminated drinking water [51] and hydrated silica from groundwater [52] also removed with EC processes successfully. López-Guzmán et al. [53] investigated the removal efficiencies in simultaneous presence were 85.68% for fluoride and approximately 100% for arsenic. Un et al. [49] determined fluoride removal from water and wastewater and the removal efficiency was 97.6%.

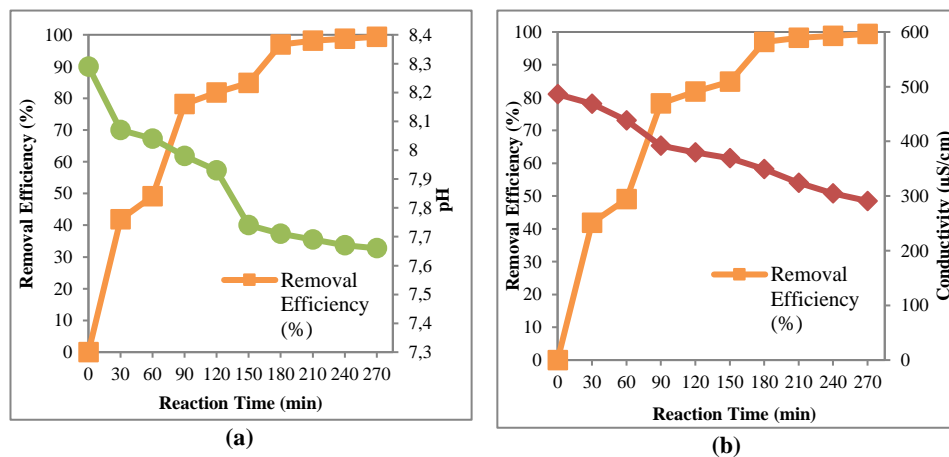


Figure 5. (a) Change in pH and F removal rate during reactor operation time, (b) Change in conductivity and F removal rate during reactor operation time.

Alcacio et al. [54] investigated arsenic removal from groundwater collected at a depth of 200 m in Central Mexico by a continuous filter press EC reactor. Arsenic removal efficiency and energy consumption were 89.6% and 0.89 kWh m^{-3} , respectively. Can et al. [55] investigated effect of some operational parameters on the arsenic removal by the batch EC reactor using iron plate electrodes. Arsenic removal efficiency and the energy consumption were 99.98% and 0.52 kWh m^{-3} . Rozales et al. [52] determined arsenic removal from groundwater and the energy

consumption of during the EC tests was 3.6 kWh m^{-3} . Uzun and İpek [56] determined the total energy consumption in the nitrate treatment of the groundwater was 0.4 kWh m^{-3} . Xu et al. [57] investigated Simultaneous removal of cadmium, zinc and manganese using electrocoagulation and the corresponding energy consumption was 2.73 kWh m^{-3} .

3.3. Fluoride adsorption on the clay mineral

The fluoride adsorption on the clay mineral depending on the contact time is shown in Figure 6. At the beginning, the amount of adsorbed fluoride raised with enhancement contact time. However, after some time, it approached a nearly constant value and reached an equilibrium within 2 hours. 36% of the initial fluoride concentration was adsorbed at the equilibrium time. It is thought that the equilibrium period was prolonged due to the thrust between the negatively charged clay particles and F ions. There was no significant change in adsorption after the 2nd hour. Adsorption on the clay mineral was fast initially then slow until a certain equilibrium time. Initial reactions are associated with diffusion of contaminants to the surface of the adsorbent.

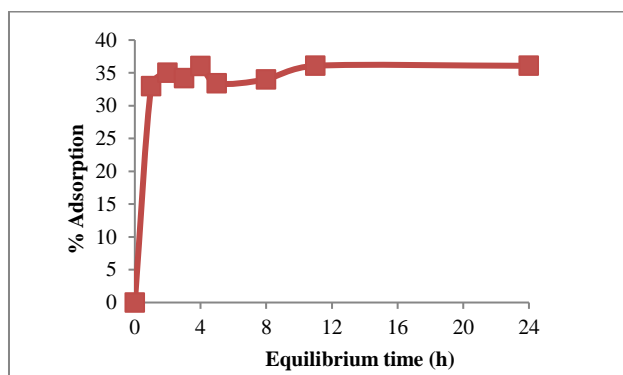


Figure 6. Time-dependent fluoride adsorption percentages on the clay mineral

In the description of adsorption data, Freundlich and Langmuir equations were used. The values of Freundlich adsorption constants of clay mineral are given in Table 5. The values of $1/n_f$ for clay mineral was <1.0 indicating the L type isotherm. Langmuir equation also displayed a good fit to experimental data for fluoride as denoted L type isotherm. Mandal and Mayadevi [58] and Sundaram et al. [59] also reached that the fluoride adsorption in clay mineral fitted well with both Langmuir and Freundlich equations. Table 6 shows the Langmuir adsorption constants for the F adsorption on the clay mineral. A small value of $1/n_f$ (<1.0) indicated a weaker physical bond between adsorbate and adsorbent representing the heterogeneous adsorbent surface. Low value for K_f (0.14) notified the low F adsorption on the clay mineral. It can be accounted by negatively charged places on the clay which made the material infertile adsorbent for anionic F. This means that negatively charged pollutants generally exhibited a few sorption on the clay materials.

Table 5. Freundlich constants for the fluoride adsorption on the clay mineral

Isotherm	Isotherm constants	Clay mineral
Freundlich Isotherm	K_f	0.14
	$1/n_f$	0.875
	n_f	1.143
	r	0.99

Table 6. Langmuir constants for the fluoride adsorption on clay and bauxite minerals

Adsorbent	Q_0	$1/Q_0$	b	$1/Q_0 * b$	r
Clay mineral	3.155	0.317	0.045	7.023	0.98

As a result, the high amount of F in groundwater in Sarım and Karataş revealed the dental fluorosis problem in the region. The removal of fluoride by electrocoagulation and adsorption methods were investigated to produce a short-path solution. Low F adsorption was found on the clay mineral. Clay material is thought to be an inefficient adsorbent for the negatively charged fluoride ions. Despite the low F removal by adsorption, about 99.4% removal efficiency was achieved in EC process at the end of 270 min. Although the electrocoagulation seems to be a high cost method, solar energy can be a good alternative to minimize the energy costs. Therefore, the electricity requirement can be supplied by photovoltaic solar panels during the long period of sunny days in the region in a year.

4. CONCLUSIONS

As a conclusion EC process can be applied successfully for the removal of fluoride in water. Efficiency of EC method depends on the amount of coagulant raised during the operation time. Produced Al^{+3} ions in EC reactor proceed as the coagulant material and removed the F in water. High cost energy disadvantages of EC method can be reduced by solar energy. Low F adsorption was found on the clay mineral. Clay material is thought to be an inefficient adsorbent for anionic species. Clay materials must be modified to enhance their adsorption potential for water defluoridation. Different modification methods can be applied on the natural materials.

Acknowledgment

This study was funded by the Scientific Research Projects Committee of Harran University, (HUBAK) under Project No. 17199. I would like to thank Gülistan Banu ÇAKMAK for her contributions to the laboratory work.

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