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Removal of Fluoride from Groundwater by Batch Electrocoagulation Process Using Al Plate Electrodes

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Abstract

Dental fluorosis cases are observed due to the high consumption of high fluoride drinking water in some parts of Anatolia. 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 showed that the concentrations in groundwater samples were above the admissible limit values for potable water (>1.5 mg/L). Objectives of this work are; to study the high fluoride in groundwater of Sarım-Karataş region, its health effects and to examine its removal efficiency from groundwater by electrocoagulation (EC). EC process including the electrodes, reactor and the power source successfully removed the fluoride from groundwater sample. F removal rate was found as ~96% at the end of 3 hour.

Key words: Fluoride, electrocoagulation, fluorosis, groundwater.

1. Introduction

One of the trace elements important for human health is fluoride (F) [1]. Fluoride is found in the human body as well as in rocks, soils, air, water, plants and animals. The maximum pollution level in drinking water for fluoride is 4 mg/L according to US EPA. The optimum dose of fluoride was found to have a protective effect on the teeth of children and adults. Low (<0.5 mg/L) and high fluoride concentrations (>1.5 mg/L) in drinking water lead to dental caries and dental stains and dental fluorosis, respectively [2]. Studies have shown that high fluoride concentration is associated with magmatic and metamorphic rocks in groundwater in different parts of the world. [3].

Fluoride is still important in preventing dental caries. However, overdose of fluoride ingestion increases the risk of dental fluorosis [4,5]. 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 [6]. In addition, high fluoride concentration may cause skeletal fluorosis and serious problems in body [7-10]. As seen in studies in some parts of Turkey, fluoride concentration of water was found high from 1.5 to 13.7 mg/L due to the volcanic rocks and geothermal sources [11-14]. Yeşilnacar (2010) has first detected excessive fluoride in groundwater and dental fluorosis cases in Sarım and Karataş villages [15,16].

There are many fluoride removal technologies today in a worldwide such as membrane processes [17], electrodialysis [18], adsorption [19,20], ion exchange [21], coagulation and electrocoagulation [22,23]. 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

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of contaminants [24]. EC technology develops as a promising alternative because it provides advantages that eliminate the disadvantages of conventional methods [25]. 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. In this study, the removal of fluoride in groundwater by EC method and its effects on human health was determined.

2. Materials and Method

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.

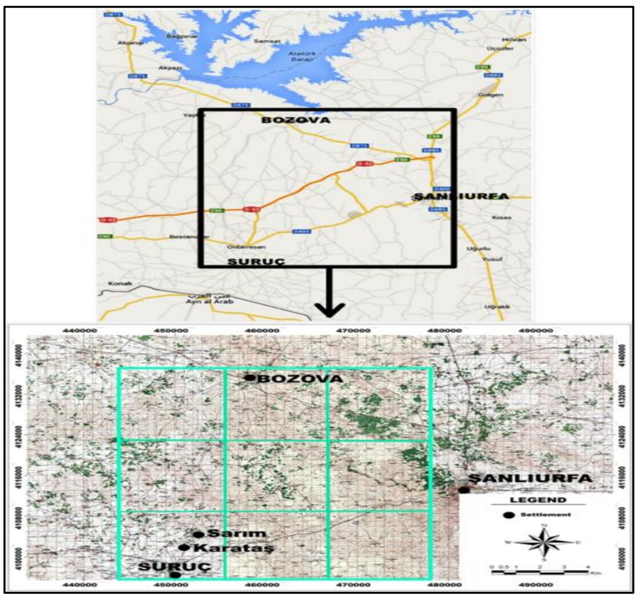

Figure 1. The location map of the studied area

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).

Ground water samples were taken from Sarım village. The characteristics of the groundwater and EC reactor are given in Table 1.

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

Parameter	**Value**
pH	8.49
Electrical conductivity (µS/cm)	468
Temperature (°C)	25
F^- (mg/L)	**1.95**
Cl^- (mg/L)	15.98

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. Al electrodes were assembled the reactor. The voltage and current were set to a desired value (5V-1A) through adjustment of the power supply and the experimental study was started at room temperature (25 ºC). The duration of the experiment was 180 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.

Figure 2. The set-up used in the study

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) [26].

Anode: $Al_{(s)} \rightarrow Al_{(aq)}^{3+} + 3e^-$ (1)

Katode: $3H_2O + 3e^- \rightarrow 1.5H_{2(g)} + 3OH^-$ (2)

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

$$Al_{(aq)}^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (3)$$

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 [9].

3. Results

3.1. Dental fluorosis in study area

In Sarım and Karataş villages, high amount of fluoride in groundwater was determined. The reason of this; Oligocene - Lower Miocene aged clayey-limestones may be found locally. In addition, fluoride ions released into water environment by dissolving F-containing minerals as a result of interaction with water are among the reasons. This theory reinforces the fact that wells to provide drinking and potable water in these two villages have been drilled in the last 10-15 years and that the age range of children with fluorosis is 7-13 [27].

Atasoy and Yesilnacar [7] 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) [15]. The amount of fluoride in ground water was between 1 and 4 mg/L. Sarım and Karataş samples were higher than the values reported by WHO (0.5-1.5 mg/L). High fluoride concentration in groundwater caused the dental fluorosis in the region.

Figure 3. Some images from the dental examinations

4. Discussion

4.1. 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. Electrocoagulation process successfully decreased the fluoride concentration below the maximum contaminant level of 1.5 mg/L (~96% removal) (Figure 4). F removal rate increased with the operation time due to the arising Al^{+3} ions by aluminum anode during the process time. Table 2 showed the EC operating conditions and energy consumption. According to the results, the energy consumption increased with the decreased conductivity [28,29]. The lowest energy consumption value (0.13 kWh/m^3) corresponded to the highest conductivity (468 µS/cm). The pH of a solution is one of the most significant parameters in EC process [30,31]. 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 7.6 and 290 µS/cm, respectively.

Table 2. The EC operating conditions

Parameter	EC Process
Electrode material	Al
Current density (mA/cm^2)	1.5
Temperature (ºC)	25
Initial pH	8.49
Final pH	7.6
Initial electrical conductivity (µS/cm)	468
Final electrical conductivity (µS/cm)	290
Operating time (min)	180
Energy consumption (kWh/m^3)	0.76
Energy consumption per kg fluoride (kWh/kg F)	466.1

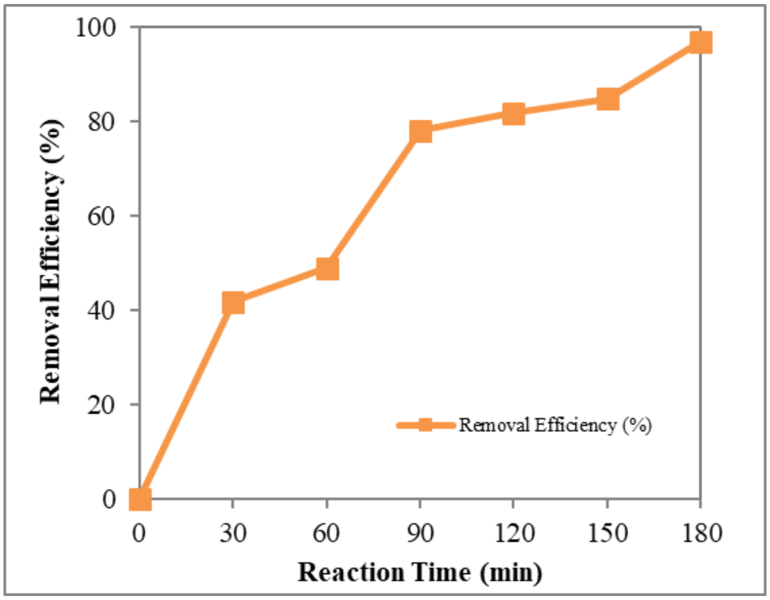

Figure 4. Change in F removal rate during reactor operation time

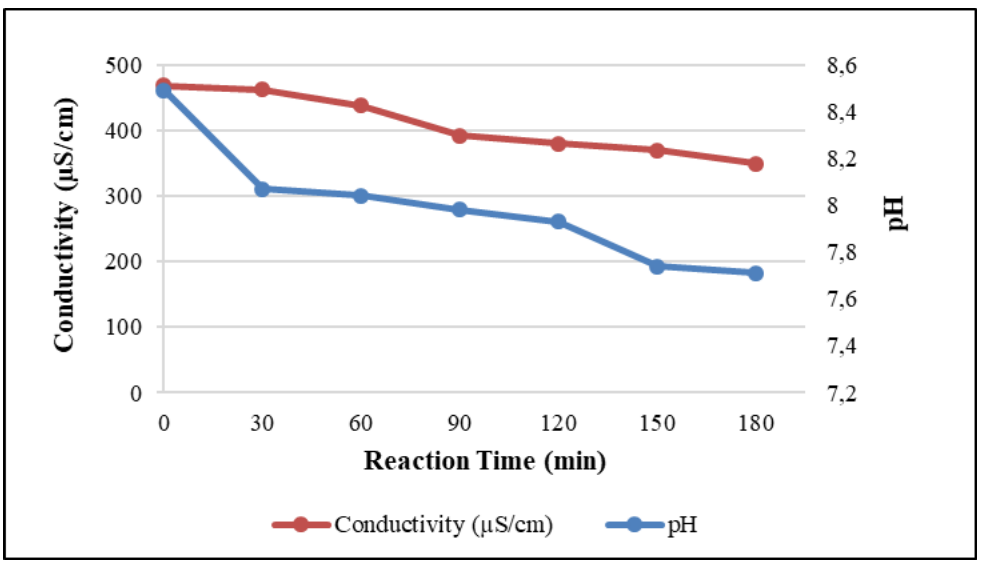

Figure 5. Change in pH and conductivity during reactor operation time

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.

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