DEFLUORIDATION OF GROUNDWATER IN CENTRAL MEXICO BY ELECTROCOAGULATION

Luna J,[a] Martinez J,[a,*] Montero C,[b] Muñiz C,[a] Ortiz J,[a] Gonzalez G,[c] Vazquez V,[d] Equihua F[e]

Coahuila, México

ABSTRACT: Electrocoagulation (EC) was used to treat groundwater contaminated with the fluoride ion (F^-). The groundwater was drawn from wells in the states of San Luis Potosi and Aguascalientes in central Mexico. Batch tests were performed using aluminium electrodes in an EC reactor. The EC response variables were the energy consumption, the electrode consumption, and the required processing time for removing F^- to the maximum permissible limit (1.5 mg L^{-1}) in water for human consumption that has been established by the World Health Organization (WHO). The sludge generated in the process was characterised using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). The results showed that EC is an effective technique for groundwater defluoridation. A reduction in the F^- concentration from 5.17 to 1.5 mg L^{-1} was achieved in 4 minutes. The energy and electrode consumption were 0.99 kW h m^{-3} and 37.36 g m^{-3}, respectively. The reflections in the XRD pattern indicated that the sludge formed consists in gibbsite $Al(OH)_3$ and calcite ($CaCO_3$).

Keywords: Defluoridation; Electrocoagulation; Groundwater.

INTRODUCTION

Groundwater contamination by the fluoride ion (F^-) occurs primarily through natural processes, such as the dissolution of the element from minerals, and industrial activities.[1-4] Fluoride has negative health effects.[5] Therefore, the World Health Organization (WHO) has set a F^- maximum permissible limit of 1.5 mg L^{-1} in water intended for human consumption.[6]

Some of the methods that are used to remove fluoride from water involve precipitation, adsorption, and ion and membrane exchange.[7-9] Among these methods, electrocoagulation (EC) is a novel water treatment that has been successfully used to treat groundwater,[10] potable water,[11] and wastewater,[2] The method offers the advantage of low sludge production and requires virtually no chemical agents.[12] In EC, an electric current is used to produce hydroxides (usually iron or aluminium) by anodic oxidation of these metals in an aqueous medium. The resulting species adsorb the pollutants found in water and are then removed using techniques such as sedimentation and filtration.[12] Previous studies have shown that EC can be used to remove F^- at efficiencies above 80%.[13] However, synthetic water was used in these studies instead of natural water and the removal of F^- from water by EC has been

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[a]Faculty of Engineering, Autonomous University of Coahuila, Blvd. Fundadores km 13 Ciudad Universitaria, C.P. 25350, Arteaga, COAH, México; [b]CINVESTAV Saltillo Unit, Av. Industrial Metalurgica 1062, Parque Industrial Saltillo-Ramos Arizpe, C.P. 25900 Ramos Arizpe, COAH, México; [c]Polytechnic University of Monclova-Frontera, Av. Las Granjas 602, C.P. 25720, Monclova, COAH, México; [d]Department of Chemical Engineering and Metallurgy, Blvd Rosales y Encinas, C.P. 83190, Hermosillo, SON, Mexico; [e]Faculty of Electric and Mechanical Engineering, Autonomous University of Coahuila, Av. Barranquilla s/n, C.P. 25750, Monclova, COAH, México. *For correspondence: Dr Jesus Fernando Martinez Villafañe, Faculty of Engineering, Autonomous University of Coahuila, Blvd. Fundadores km 13 Ciudad Universitaria, C.P. 25350, Arteaga, COAH, México; E-mail: mvjfer@gmail.com.

shown to decrease with the presence of other ions.[13,14] Therefore, because of the ions present in groundwater, the EC treatment of natural groundwater produces different results than the EC treatment of synthetic water.

For this reason, in this research study, we systematically investigated the use of EC to treat natural groundwater that was contaminated with F^- to comply with the WHO maximum permissible limit of 1.5 mg L^{-1}. The reactor performance was evaluated in terms of the response variables: the treatment time (t), the electric power consumption (E), and the electrode consumption (w). Previous studies have shown that the most significant factor in EC treatment is the type of flow in the reactor.[11] Therefore, tests were performed to vary the flow type in the reactor under the following conditions: (i) free convection (L), (ii) forced convection with water flow (A), and (iii) forced convection with air flow (G).

The reactions for the removal of F^- in water by EC using aluminium electrodes are given below:[15]

anodic reaction

$$Al_{(s)} \rightarrow Al^{3+} + 3e^- \qquad (1)$$

cathodic reaction

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

In the space between the electrodes, the aluminium ions react with the hydroxyl ions that are produced at the cathode to form aluminium hydroxide as follows:[15]

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_{3(s)} \qquad (3)$$

The aluminium hydroxides form flocs that remove F^- and are precipitated during the treatment process. The removal of F^- by the $Al(OH)_3$ flocs proceeds via an ion exchange reaction:[15]

$$Al(OH)_3 + xF^- \rightarrow Al(OH)_{3-x}F_x + xOH^- \qquad (4)$$

MATERIALS AND METHODS

EC reactor: EC was performed in a reactor that could be operated continuously and in batch mode. In this study, the EC tests were conducted in batch mode because the equipment could be operated more easily and lower maintenance was required as no moving parts were involved.[11] In addition, the studies could be conducted at different flow rates, such as using the free convection rate (L), or creating forced convection to ensure uniform mixing in the reactor. by using either water flow (A) or air flow (G). The volume of the reactor was 1.2 L. The reactor consisted of rectangular plates that were formed of aluminium electrodes (Al) 6061 with dimensions of 10 × 14 × 0.635 cm for the height, width, and thickness, respectively. These plates were connected in a bipolar mode and oriented vertically. This type of internal orientation has been shown to promote circulation in the reactor.[11] Figure 1 is a scheme of the reactor configuration. The water to be treated was fed in at the top of the reactor and samples were withdrawn from the bottom of the reactor at the treatment times of interest in the study. The power supply consisted of a *Vimar* potentiostat-galvanostat, where the electrical contact of the terminal electrode was formed at the upper section of the electrodes. Uniform mixing was achieved throughout the reactor using forced convection, which was facilitated by water flow (A), using 2 *via aqua 40* multistage submersible pumps that each provided a liquid flow of 2.5 L min^{-1}. When forced convection was facilitated by air flow (G), an air pump *Azoo 9500* with a variable flow from 1.6 L min^{-1} was used. The discharge was connected to two porous membrane diffusers that were located at the base of the reactor that insufflated bubbles with diameters of 2 mm. Thus, the bubbles covered the entire inter-electrode area, ensuring a uniform concentration distribution of the species throughout the reactor.[10]

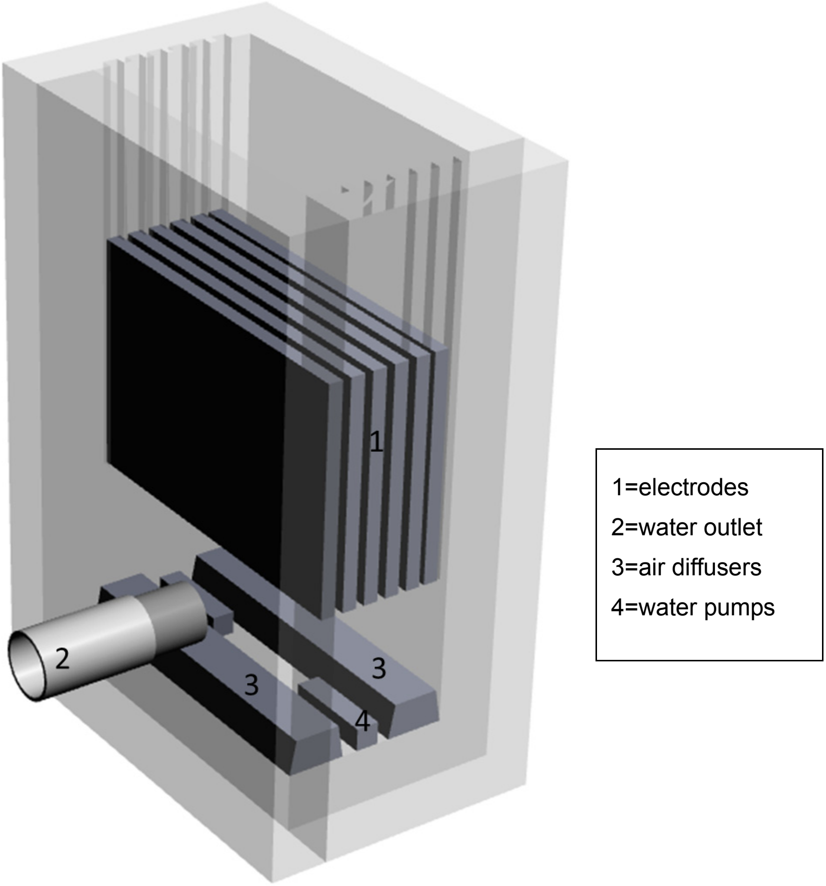


Figure 1. Scheme of the EC reactor: (1) electrodes, (2) water outlet, (3) air diffusers, and (4) wate pumps.

Groundwater and generated solids: Samples were taken from water wells intended for human consumption in various parts of central Mexico to identify areas with F^- contamination. Subsequently, contaminated water was drawn from wells in the states of San Luis Potosi and Aguascalientes in central Mexico.

To study the kinetics of F^- removal, samples were withdrawn at different times during the EC process, and filtered using cellulose paper with a pore size of 2.5 μm to separate the sludge formed in the water. The residual F^- concentration in the filtered water was analysed.

A potentiometric technique was used to analyse F^- using *Orion 9609* ion selective electrodes. An ionic strength adjustment solution *TISAB II* was used to avoid interference from other ions during the analysis of F^-. The pH was measured with a *LPH430T Tacussel* pH meter, and the conductivity (k) was analysed using a *Condutronic* conductivity meter.

The optimal operating conditions for the treatment time (t), the consumed energy (E), and the electrode consumption (w) for the EC reactor were determined in previous studies.[10] Therefore, the experiments were performed using an inter-electrode distance d = 3 mm, a current density i = 3.0 mA cm^{-2}, and a ratio of the exposed electrode area to the treated water volume A/V = 0.466 cm^{-1}. The flow type in the reactor is the most significant factor in the EC process.[10] The flow type was changed by using either (i) free convection (L) or (ii) forced convection, with the force coming from water flow (A) or air flow (G).

RESULTS AND DISCUSSION

Chemical analysis of collected samples: Tables 1 and 2 summarise the results of the chemical analysis of groundwater samples that were taken from the wells in central Mexico.

Table 1. Chemical analysis of collected groundwater for pH, conductivity (μS cm^{-1}), and fluoride (F) and aluminium (Al) content (mg L^{-1})

State	Region or place	pH	k (μS cm^{-1})	Chemical composition (mg L^{-1})	
				F	Al
San Luis Potosí	Villa de Arriaga	7.69	591	5.11	<0.05
Aguascalientes	El Llano	7.89	643	3.81	<0.05
Aguascalientes	Calvillo	7.82	376	2.76	<0.05

Table 2. Chemical analysis of collected groundwater for arsenic (As), cadmium (Cd), lead (Pb), and chromium (Cr) content (mg L^{-1})

State	Region or place	Chemical composition (mg L^{-1})			
		As	Cd	Pb	Cr
San Luis Potosí	Villa de Arriaga	0.012	<0.003	<0.010	<0.020
Aguascalientes	El Llano	<0.010	<0.003	<0.010	<0.020
Aguascalientes	Calvillo	<0.010	<0.003	<0.010	<0.020

Tables 3 and 4 show the results of the chemical analysis of other elements that were present in the groundwater. After these samples were analysed, experiments were performed on the same samples to evaluate the response of the developed EC process to determine the feasibility of using this method for F^- removal.

Table 3. Chemical analysis of collected groundwater for calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+) content (mg L^{-1})

State	Region or place	Chemical composition (mg L^{-1})			
		Ca^{2+}	Mg^{2+}	Na^+	K^+
San Luis Potosí	Villa de Arriaga	15.94	3.86	34.13	15.29
Aguascalientes	El Llano	11.11	7.44	41.1	9.8
Aguascalientes	Calvillo	12.77	7.4	47.89	12.48

Table 4. Chemical analysis of collected groundwater for silcon dioxide (SiO_2), sulphate (SO_4^{2-}), and chloride (Cl^-) content (mg L^{-1}) and total hardness

State	Region or place	Chemical composition (mg L^{-1})			Total hardness
		SiO_2	SO_4^{2-}	Cl^-	
San Luis Potosí	Villa de Arriaga	35.78	50.01	51.12	49.50
Aguascalientes	El Llano	9.8	93.22	14.19	5.13
Aguascalientes	Calvillo	86.72	14.76	5.97	50.42

Figure 2 shows the evolution of F^- removal from groundwater using EC for free convection and convection forced by water flow or air flow.

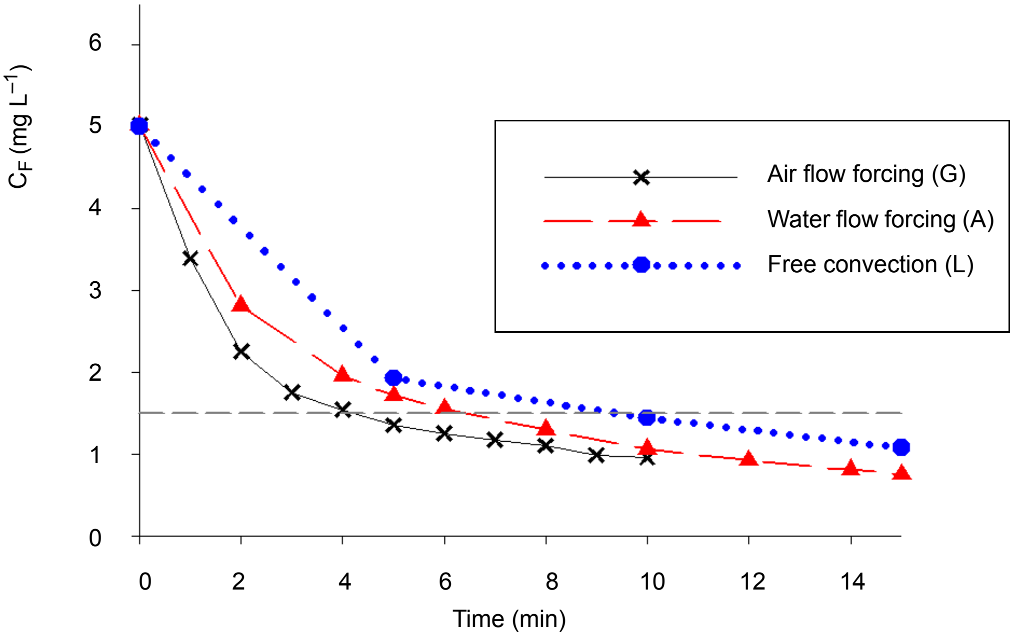


Figure 2. Fluoride ion (F^-) removal from groundwater (C_{F0} = 5.17 mg L^{-1}) as a function of the treatment time for different flow types: free convection (L), convection forced with water flow (A, and convection forced with air flow (G).

Figure 2 shows that when air flow was supplied to the EC reactor, F^- removal was relatively rapid in the first 2 min. This result was obtained because the air flow rapidly produced homogeneous mixing in the EC reactor.[10] Thus, reactions (1)–(4) also occurred rapidly. However, this effect diminished with time, and the WHO concentration limit was attained in 4 min. Using water flow to generate forced convection in the EC reactor increased the treatment time to 6 min, and the processing time increased to 9 min using free convection. These results were obtained because it took longer to achieve uniform mixing in the EC reactor under these conditions than when air flow was used.[10] Note, however, that these treatment times are lower than those reported in the literature.[13]

Energy consumption (E): The energy (*E*) consumed during the EC process is related to the voltage drop across the reactor (*U*), the applied current (*I*), and the treatment time (*t*), as given by the following equation:[10]

$$E = IUt \tag{5}$$

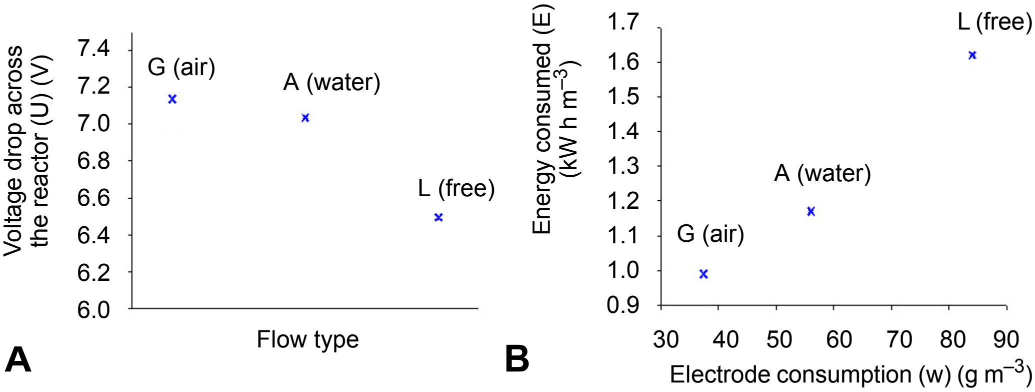
If required, the value for *E* can be obtained in kilowatt hours (kW h) by dividing the result obtained using equation (5) by 1000. This energy consumption for F^- removal is added to the energy consumption of the devices that are used to produce the liquid motion. Thus, we calculated that the energy required for forced convection was 6 Wh for water flow (A) and 3 Wh for air flow (G).[10]

Electrode consumption (w): We used the following equation to calculate the consumption of the electrodes for each water treatment:[10]

$$w = \frac{ItM}{nF} \tag{6}$$

where *n* is the number of electrons transferred, *F* is the Faraday constant, and *M* is the atomic mass. The equation above shows that the electrode consumption is directly proportional to the treatment time and the current supplied.

Figures 3A and 3B show, respectively, the effect of the flow pattern on (i) the voltage drop and (ii) the energy and electrode consumption during the required treatment time to obtain a F^- concentration = 1.5 mg L^{-1} in groundwater with an initial F^- concentration 5.17 mg L^{-1}



Figures 3A and 3B. Effect of flow type [free convection (L), convection forced with water flow (A), and convection forced with air flow (G)] on: 3A: voltage drop across electrodes and 3B: energy and electrode consumption for fluoride ion (F^-) removal from groundwater by electrocoagulation (EC) treatment (C_{F0} = 5.17 mg L^{-1}).

Figure 3A shows that the lowest voltage drop (U) was obtained using free convection. This result was attributed to the absence of large liquid motions between the species in solution, which allowed unimpeded current flow between the electrodes. The converse situation was observed using forced convection. In this case, uniform mixing and the rapid motion of the species resulted in interference between the current lines in the system, thereby increasing U. The forced convection produced by the air flow produced the highest increase in U, primarily because the space occupied by the bubbles interrupted the lines of current.[10] Figure 3B shows that the forced convection caused by the air flow reduced the power consumption (E) (0.99 kW h m^{-3}) and the electrode consumption (w) (37.36 g m^{-3}) because the reaction kinetics were faster and less processing time was therefore required. However, using other flow types increased the E and w values. The E value increased by approximately 18% (E = 1.17 kW h m^{-3}) when forced convection was created exclusively by water flow (A) and more significantly by approximately 64% (E = 1.62 kW h m^{-3}) using free convection (L). The electrode consumption also increased by approximately 50% (w = 56.04 g m^{-3}) when convection was created using water flow (A) and by approximately 125% (w = 84.06 g m^{-3}) when free convection (L) was used. These results show that the use of air flow maximised the process efficiency.

Figure 4 shows the kinetics of F^- removal at groundwater contaminant concentrations of 5.17, 3.86, and 2.77 mg L^{-1}.

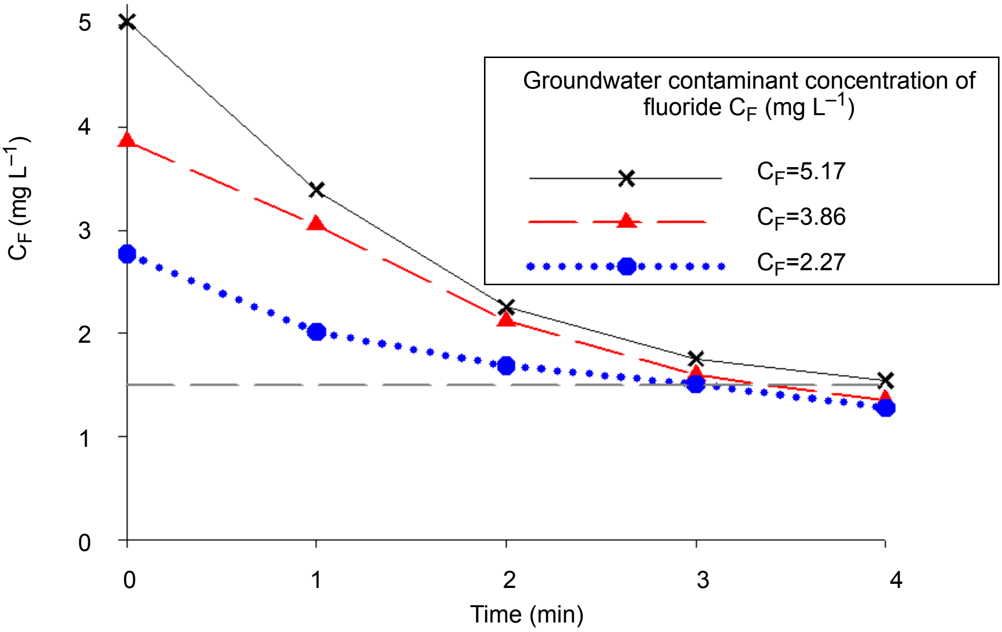
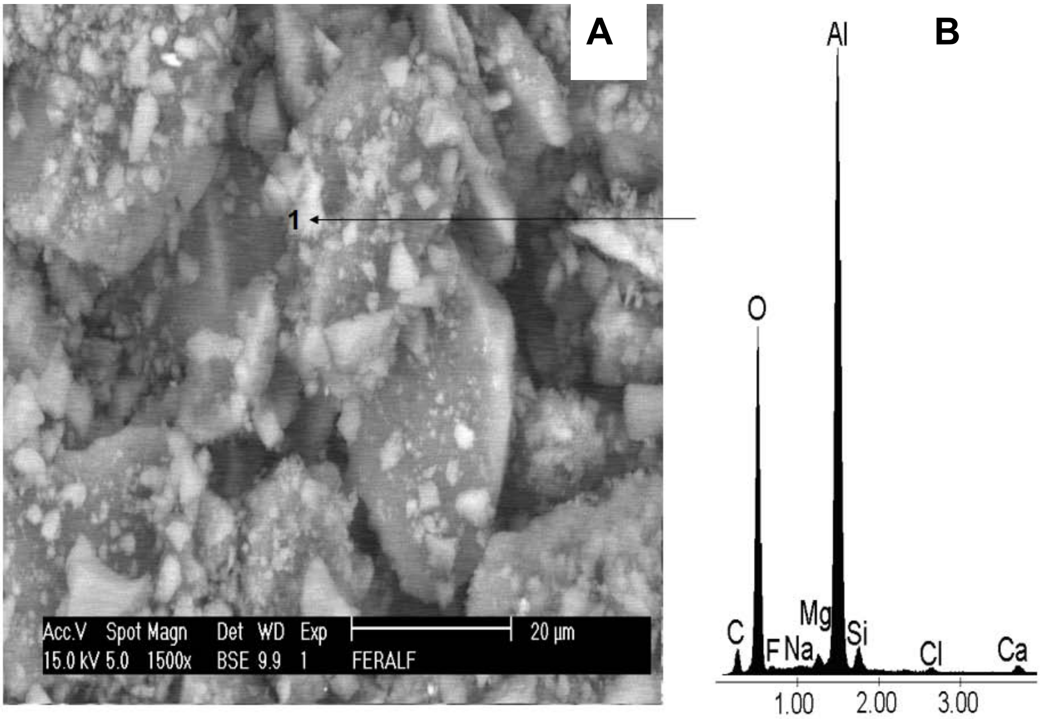


Figure 4. Kinetics of fluoride ion (F^-) removal in groundwater at the contaminant concentrations of 5.17, 3.86, and 2.27 mg L^{-1}.

Figure 4 shows that the time to reach the WHO limit was decreased by decreasing the initial F^- concentration. For C_{F0} = 5.17, 3.86, and 2.77 mg L^{-1}, the limit was reached in approximately 4, 3.2, and 3 min, respectively. However, the figure also shows that the removal kinetics decreased as the initial F^- concentration decreased. Therefore, we concluded that contaminants were rapidly adsorbed onto the generated flocs at high F^- concentrations and that the process was slowed down by decreasing the F^- concentration. Measurements of calcium concentration (Ca) were performed in the treated groundwater (C_{F0} = 5.17, 3.86, and 2.77 mg L^{-1}) resulting in values of 10.97, 7.59, and 8.72 mg L^{-1}, respectively. Similarly analyses of the aluminium (Al) levels were performed in the treated groundwater and they were below 0.05 mg L^{-1} (limit detection of inducted coupled plasma ICP). This was attributed to the minimal solubility of aluminum species at this pH.[16]

Characterisation of generated sludge: The sludge generated by the removal of F^- from groundwater by EC, was separated from the treated water using cellulose filter paper with a pore size of 2.5 µm, followed by drying for 2 hr at 100ºC in a *Barnstead Thermolyne 62700*. The morphology of the resulting dry sludge was characterised by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) using a *Philips XL30* microscope at 20 kV, and the phases of the sludge were determined using X-ray diffraction (XRD).

The morphological information on the solid samples was obtained from SEM. Figure 5A is a SEM image of the sludge formed during F^- removal from groundwater by EC.



Figures 5A and 5B. 5A: Scanning electron microscopy (SEM) micrograph at 1500× of the sludge formed during fluoride ion (F^-) removal from groundwater by electrocoagulation (EC) and 5B: energy-dispersive X-ray spectroscopy (EDS) spectrum from the point analysis in region 1 (indicated by arrow).

As can be seen in this figure, the sludge formed consists of angular crystals with sizes of approximately 20 µm and smaller crystals of approximately 3 to 6 µm adsorbed onto their surfaces. The EDS spectrum shows the composition of the sludge (Figure 5B). This spectrum shows that the sludge primarily consisted of the elements of Al and O. Table 5 shows the chemical composition of the sludge in weight percentages of each element.

Table 5. Chemical composition (weight %) of sludge generated after fluoride ion (F^-) removal by electrocoagulation (EC)

	Element							
	O	F	Na	Mg	Al	Si	Cl	Ca
Weight %	41.78	0.72	0.4	1.3	50.9	2.93	0.6	1.54

Figure 6 shows the XRD patterns of the sludge generated during the EC process and separated by filtration from the groundwater.

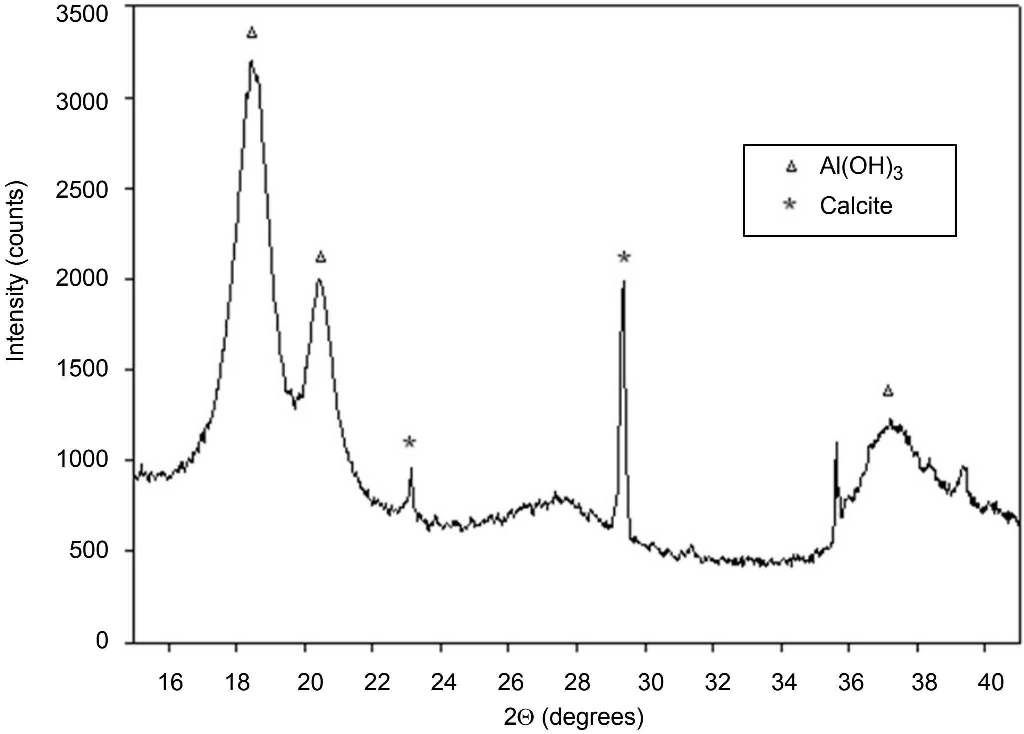


Figure 6. X-ray diffractogram of the sludge formed during fluoride ion (F^-) removal from groundwater by electrocoagulation (EC).

In Figure 6, the primary reflections in the XRD pattern are indicated by the triangular symbols at 2Θ = 18.43° (002), 20.41° (110), and 37.46° (021), which are consistent with those expected for the $Al(OH)_3$ phase (gibbsite). The parameters of the unit cell corresponded to the monoclinic structure, a = 8.68 Å, b = 5.07 Å, c = 9.72 Å, and β = 94.57°. The gibbsite structure consists of stacked octahedral sheets of aluminium hydroxide. The reflections marked with asterisks at 2Θ = 23.00° and 29.40° were associated with the (012) and (104) planes respectively, which are consistent with those expected for the ($CaCO_3$) phase (calcite). Calcium compounds, in this case, calcite ($CaCO_3$), have a solubility constant of 1×10^{-8} and can easily precipitate onto the $Al(OH)_3$ flocs.[17]

CONCLUSIONS

The results of this study demonstrate that groundwater defluoridation can be performed successfully using EC. F^- removal was maximised by supplying air to the EC reactor. The maximum F^- limit (1.5 mg L^{-1}) in water intended for human consumption was achieved in 4 min for an energy consumption of 0.99 kW h m^{-3} and an electrode consumption of 37.36 g m^{-3} which represents a cost in Mexico of US$0.04 in electricity and US$0.13 in electrodes, for a total of US$0.17 per m^3 of treated groundwater. The reflections in the XRD pattern indicated that the sludge formed consists in gibbsite $Al(OH)_3$ and calcite ($CaCO_3$). The EDS spectrum not only confirmed the presence of F, Al, O, and Ca in the generated sludge but also a low ratio of F^-/aluminium hydroxide and Ca/aluminium hydroxide, therefore the sludge generated can be converted to alum for use elsewhere. SEM images showed that the aluminium hydroxides have an amorphous morphology size of approximately 20 µm and smaller particles ranging from 3 to 6 µm were adsorbed onto the surfaces of the aluminium hydroxide.

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