

## Research article

# Fluoride removal from natural volcanic underground water by an electrocoagulation process: Parametric and cost evaluations

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## ABSTRACT

Excessive fluoride content in groundwater can cause serious risks to human health, and sources of groundwater intended for human consumption should be treated to reduce fluoride concentrations down to acceptable levels. In the particular case of the island of Tenerife (Canary Islands, Spain), the water supply comes mainly from aquifers of volcanic origin with a high content of fluorides that make them unacceptable for human consumption without prior conditioning treatment. The treatments that generate a high rejection of water are not acceptable because water is a scarce natural resource of high value. An electrocoagulation process was investigated as a method to treat natural groundwater from volcanic soils containing a hazardously high fluoride content. The operating parameters of an electrocoagulation reactor model with parallel plate aluminum electrodes were optimized for batch and continuous flow operations. In the case of the batch operation, acidification of the water improved the removal efficiency of fluoride, which was the highest at pH 3. However, operation at the natural pH of the water achieved elimination efficiencies between 82 and 92%, depending on the applied current density. An optimum current density of 5 mA/cm<sup>2</sup> was found in terms of maximum removal efficiency, and the kinetics of fluoride removal conformed to pseudo-second-order kinetics. In the continuous-flow operation, with the optimal residence time of 10 min and a separation of 0.5 cm between the electrodes, it was observed that the current density that would be applied would depend on the initial concentration of fluoride in the raw water. Thus, an initial fluoride concentration of 6.02 mg/L required a current density > 7.5 mA/cm<sup>2</sup> to comply with the legal guidelines in the product water, while for an initial concentration of 8.98 mg/L, the optimal current density was 10 mA/cm<sup>2</sup>. Under these operating conditions, the electrocoagulation process was able to reduce the fluoride concentration of natural groundwater to below 1.5 mg/L according to WHO guidelines with an operating cost between 0.20 and 0.26 €/m<sup>3</sup> of treated water.

## 1. Introduction

The threat to human health caused by excessive fluoride intake is well documented (Kanduti et al., 2016; Ozsvath, 2008). Long-term consumption of water with fluoride concentrations above 1.5 mg/L can cause fluorosis, a disease that affects especially bones and teeth (World Health Organization, 2001). Fluorine can be present in natural groundwater in volcanic areas from two main sources. First, the filtration of surface rain water through rocky material of volcanic origin causes its fluorinated minerals to enter the underground water

(D'Alessandro, 2006; Custodio et al., 2016). In addition, areas with underground volcanic activity have high concentrations of hydrofluoric acid in the gaseous emissions. These, when in contact with water, contribute to increase the concentration of fluoride (D'Alessandro, 2006; Ayooob and Gupta, 2006). As for the Canary Islands, an archipelago of volcanic origin formed by seven main islands (see Fig. 1), groundwater is the main natural source of water supply (Custodio et al., 2016). In the northern region of the island of Tenerife, mainly in the municipalities of La Guancha, Icod de los Vinos and San Juan de la Rambla, fluoride amounts higher than 7 mg/L are recorded (Hardisson

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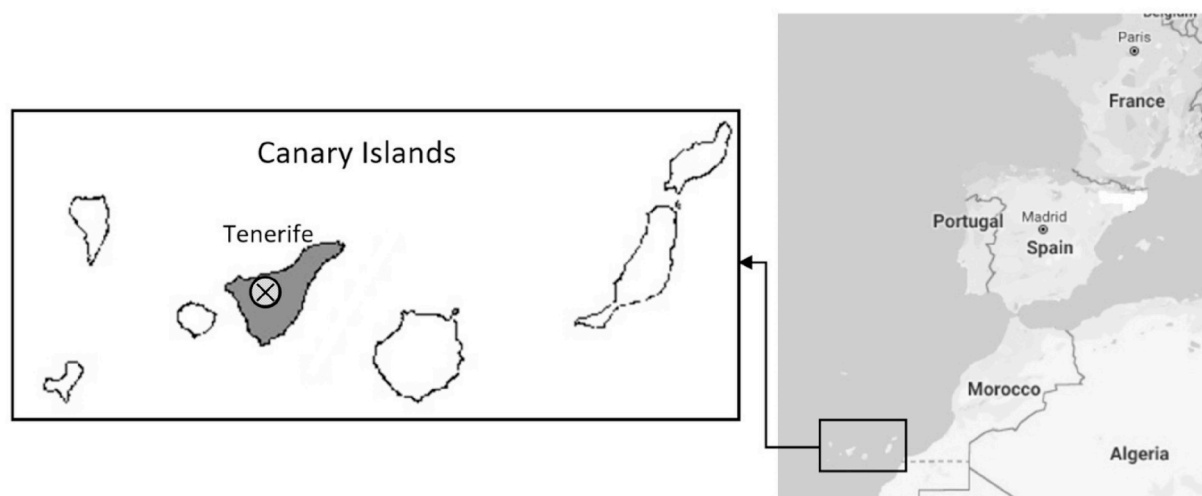


Fig. 1. Location of the Canary Islands and the study area (⊗).

et al., 2001). This is precisely the geographical area where the main sources of water are found, and this water is distributed to a large part of the island's population. This fact implements the need for a water treatment to reduce the fluoride contents to those established by legislation that can be used for human consumption (EU Directive, 1998; Real Decreto 140, 2003).

The conditioning of waters with a high fluoride content to comply with the reference values established by regulations can be done in different ways. Table 1 reviews the main methods for the elimination of fluorides in water described in the scientific literature. They are classified according to the technology used, and the most relevant characteristics of the processes are provided. The techniques that have lower costs are based on absorption/ionic exchange techniques (i.e., those employing ashes, bone, and crushed bone as absorbents), although they exhibit low fluoride removal efficiencies. In contrast, the largest fluoride removals are obtained with techniques using activated carbon or zeolites, and especially for membrane-based methods such as electrodialysis, reverse osmosis and membrane bioreactors (MBRs), although they present the highest operation costs. Currently, extensive research focuses on membrane design to improve the performance of the process in order to reduce the high costs associated to membrane operation (Krzeminski et al., 2017). The reduction of microbial origin fouling should contribute to longer service life for the MBR (Sepehri and Sarrafzadeh, 2018) and, eventually, facilitate its application for fluoride mitigation.

When considering water losses during treatment, they represent approximately 1–2% for most techniques, but can reach 20–30% in electrodialysis treatments, and 40–60% in reverse osmosis. Different drawbacks are also associated with the various methods, the most important being turbidity, arsenic content or alkalinity of the samples. Alternatively, electrocoagulation is a technology used for the treatment of urban (Chellam and Sari, 2016; Tian et al., 2016) and industrial wastewaters (Hu et al., 2008; Khaled et al., 2014), particularly from the textile (Ahmed et al., 2012; Khandegar and Saroha, 2013), photovoltaic solar cell (Drouiche et al., 2012; Palahouane et al., 2015), and semiconductor (Aoudj et al., 2015) industries. In addition, some reports have explored the potential of this technique for the conditioning of water for human consumption, especially in regard to the elimination of fluoride (Bennajah et al., 2009; Battula et al., 2014; Govindan et al., 2015) or arsenic (Lacasa et al., 2013; Omwene et al., 2019). Compared to the techniques listed in Table 1, this procedure exhibits a high efficiency of fluoride removal in the case of a continuous flow reactor

(Emamjomeh and Sivakumar, 2009), easy operation at a relative cost, and the possibility of using a fully automated system (Chen, 2014).

Electrocoagulation is a process in which colloids are destabilized due to the application of an electric field between the electrodes of an electrolytic cell (coagulation by polarization), or due to the action of coagulation agents resulting from the oxidation of an anode. The simplest electrolytic cell consists of two electrodes, an anode, where the metal oxidation occurs, and a cathode, where the reduction of a series of electrolytic components occurs. The ionic species formed in the electrodes destabilize the charges of the contaminating particles present in the water. When these charges are balanced, the physical-chemical processes that keep the particles in suspension disappear, thus allowing the formation of aggregates, and initiates the coagulation process. Hydrolysis, electrolysis, ionization and formation of free radicals are the relevant reactions that pollutants can experience at this stage (Hakizimana et al., 2017).

It is recognized that three stages are involved in the electrocoagulation process: formation of the coagulant by oxidation of the metal at the anode, destabilization of pollutants and emulsions and, finally, formation of flocs by either aggregation of contaminant particles or adsorption of the contaminant on the coagulant. The most influential factors that determine and control the reactions in the system and the formation of the coagulant are: the nature and concentration of the pollutants (Zhu et al., 2007), pH (Sivakumar and Emamjomeh, 2005; Emamjomeh and Sivakumar, 2006), distance between electrodes (Emamjomeh and Sivakumar, 2006), and applied charge density (Emamjomeh and Sivakumar, 2006). For the removal of fluoride, aluminum is the only metal used as an anode, whereas both aluminum and iron can be used for the cathode, the latter often employed to reduce costs (Khandegar and Saroha, 2013). Although several electrocoagulation reactor configurations are proposed for fluoride removal (i.e., filter-press type reactors, ascending flow reactors, circular or rectangular base, batch type, continuous flow, etc.), they were laboratory scale reactors in all cases. To our knowledge, the only functioning electrocoagulation reactor was described by Andey and coworkers, where water treatment plants were installed for human consumption, powered by solar panels, to supply treated water to small populations in India (Andey et al., 2013).

In this work, we evaluated and optimized the operation of an electrocoagulation reactor that uses aluminum electrodes for the removal of fluorides from groundwater of volcanic origin in the north of the island of Tenerife, the most populated island in Spain with almost 1

**Table 1**  
Classification of fluoride remediation technologies for water.

Technique	References	Efficiency (%)	Water loss (%)	Load/dose	Cost	Strengths	Weaknesses
<b>Methods based on precipitation processes</b>							
Aluminum	Ayoob et al. (2008)	90	1–2	150 mg/(mg F <sup>-</sup> )	Medium-High	Established procedure	Sludge formation Acidic product water Occurrence of residual Al <sup>3+</sup>
Lime	Ayoob et al. (2008)	> 90	1–2	30 mg	Medium-High	Established procedure	Sludge formation Alkalized product water
Nalgonda	Bhatnagar et al. (2011)	70–90	1–2	–	Medium-High	Easiness of operation	High concentration of residual Al <sup>3+</sup> (2–7 mg/L)
<b>Methods based on adsorption and/or ionic exchange processes</b>							
Activated charcoal	(Ayoob et al., 2008; Singh et al., 2016)	> 90	1–2	Variable	High	Adsorption load 3–5 times greater than conventional activated coal	pH change after treatment
Charcoal	Bhatnagar et al. (2011)	70	1–2	300 (mg F <sup>-</sup> )/kg	Low-Medium	Produced on site	Requires KOH
Zeolite	Wambu et al. (2016)	–	1–2	0.36–0.54 mg/(g F <sup>-</sup> )	High	Fluoride adsorption over a wide range of water conditions	Low capacity
Ashes	Ayoob et al. (2008)	60–70	1–2	80 (mg F <sup>-</sup> )/kg	Low	Produced on site	Low capacity Show operation Interference by hardness, silica and boron, etc.
Activated alumina	Rao (2003)	85–95	1–2	800 mg/(mg F <sup>-</sup> )	Medium	Good efficiency Removal of As	Big influence of pH on efficiency, thus requiring pH adjustment
Bones	Jadhav et al. (2015)	Low	1–2	900 (mg F <sup>-</sup> )/m <sup>3</sup>	Low	Produced on site	Better for the removal of F than As
<b>Methods based on membrane operation</b>							
Electrodialysis	Tahaik et al. (2006)	85–95%	20–30	High	Very high	Higher efficiencies than other membrane-based techniques Flexibility to deal with seasonal variability in the raw waters	High water losses High energy consumption
Reverse osmosis	(Jadhav et al., 2015; Litter et al., 2010)	76–95%	40–60	High	Very high	Removal of As	Small water recovery ratios (typically 10–20%) High energy consumption

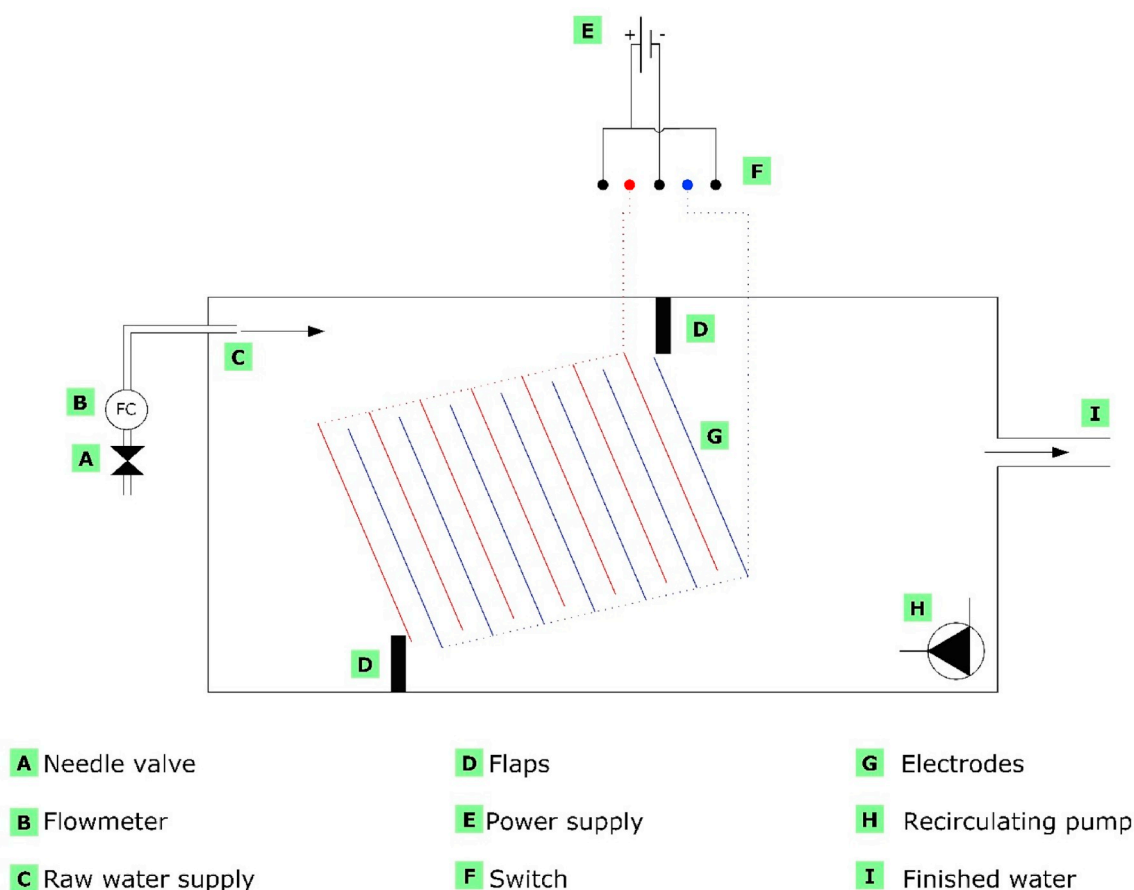


Fig. 2. Sketch of the EC reactor employed in this work.

Table 2

Experimental conditions of the electrocoagulation operation.

Parameter	Variability range
Current density (mA/cm <sup>2</sup> )	3–15
Half-period of polarity change (s)	30–120
Distance between the electrodes (cm)	0.5
Initial pH	1.04–11.20
Initial [F <sup>-</sup> ] (mg/L)	6.02–8.98
ΔV (V)	0.73–24.20

Table 3

Average chemical composition of the raw water.

Cations			Anions		
	meq/L	mg/L		meq/L	mg/L
Calcium	0.99	19.80	Carbonate	0.00	< 0.25
Magnesium	5.89	71.60	Bicarbonate	23.80	1453
Potassium	2.21	86.40	Sulfate	1.00	48
Sodium	17.40	401	Chloride	0.62	22
Aluminum		< 0.01	Nitrate	0.08	5.2
pH		7.2	Nitrite	0.00	< 0.1
Conductivity (mS/cm @ 25 °C)		2140	Phosphate	0.03	1.0
			Fluoride	0.43	8.1

million inhabitants and more than 5 million visitors per year. The main goal of this work was to reduce the fluoride concentration of the natural groundwater to below 1.5 mg/L according to WHO guidelines with competitive operating costs. The experiments were designed and carried out with natural gallery water with a high concentration of fluorides, controlling the final quality of the treated water and operating costs. The technical feasibility of the proposed system was verified at

Table 4

Performance of the EC reactor in batch operation. Operation conditions of the EC reactor: initial pH, 9.14; current density, 5 mA/cm<sup>2</sup>; distance between the electrodes, 5 mm.

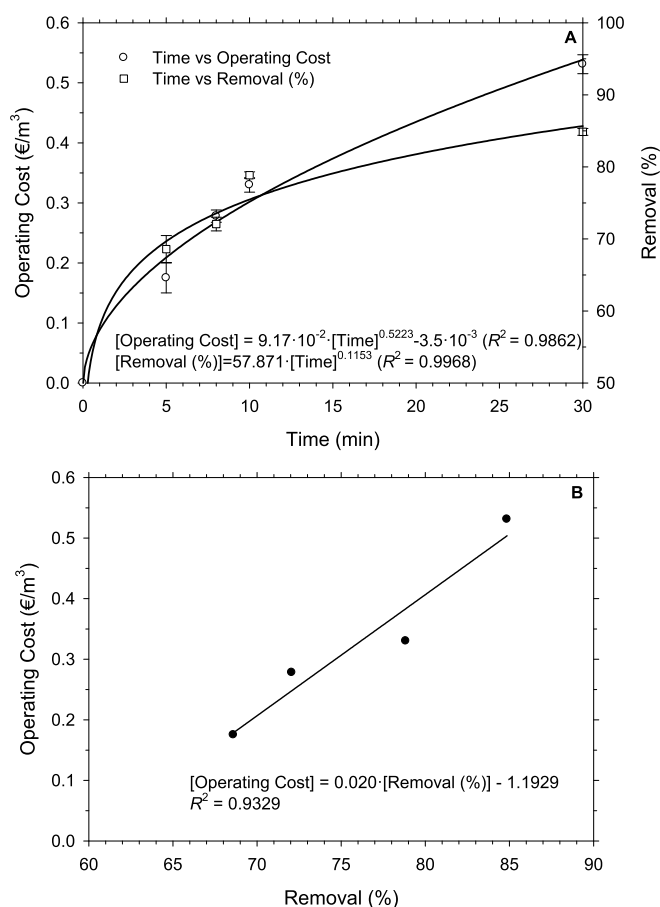
t (min)	[F <sup>-</sup> ] <sub>i</sub> (mg/L)	[F <sup>-</sup> ] <sub>f</sub> (mg/L)	Removal (%)	Voltage drop (V)	Operating Cost (€/m <sup>3</sup> )
5	8.63	2.71	68.60	0.5	0.175
8	8.63	2.41	72.07	0.8	0.278
10	8.63	1.9	78.84	1	0.330
30	8.63	1.36	84.86	1.2	0.531

the laboratory level and the operation parameters of the reactor were defined and optimized.

## 2. Experimental procedure

### 2.1. Experiment setup

The electrocoagulation process was performed in a container of 2 L capacity, with dimensions of 5.5 cm × 15 cm × 24.25 cm. The physical and hydrodynamic design of the reactor was optimized in a previous work (Betancor-Abreu et al., 2019). An immersion pump was placed inside the reactor, which allowed proper agitation of the liquid phase to be adjusted throughout the test. The electrode assembly consisted of 14 aluminum plates of 5 cm × 12 cm in size, with a separation of 5 mm between them. The electrodes were alternately arranged for connection to the power unit as shown in Fig. 2. Prior to assembly into the electrocoagulation reactor, the aluminum plates were subjected to a cleaning and conditioning process according to ASTM G1-03(2017)e1, and then stored in sealed plastic bags until use.



**Fig. 3.** Performance of the EC reactor in batch operation: A) Evolution of the operating cost and percentage of fluoride removal; B) operating cost vs. fluoride removal. Operating conditions: initial  $F^-$  concentration, 8.63 mg/L; applied current density, 5 mA/cm<sup>2</sup>; distance between the aluminum electrodes, 5 mm. Error bars account for the standard deviation.

**Table 5**

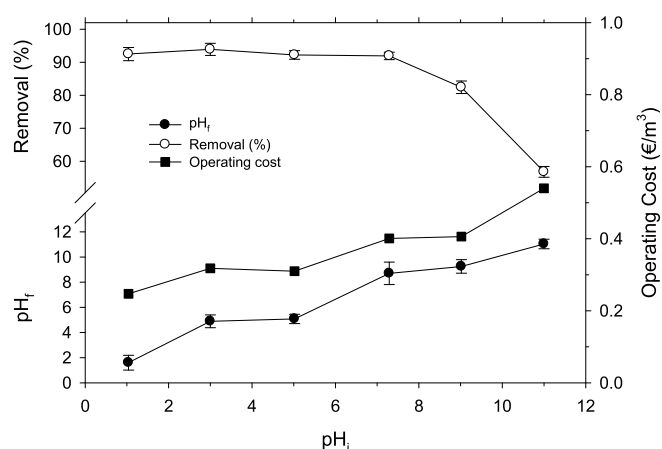
Influence of initial water pH on the electrocoagulation process in batch regime. Operation conditions of the EC reactor: current density, 5 mA/cm<sup>2</sup>; distance between the electrodes, 5 mm.

pH <sub>i</sub>	pH <sub>f</sub>	[F <sup>-</sup> ] <sub>i</sub> (mg/L)	[F <sup>-</sup> ] <sub>f</sub> (mg/L)	Removal (%)	Voltage drop (V)	Operating Cost (€/m <sup>3</sup> )
1.04	1.72	7.06	0.53	92.49	1.34	0.247
3.00	4.89	7.06	0.43	93.91	2.13	0.318
5.02	5.08	7.06	0.55	92.21	2.04	0.310
7.29	8.94	7.06	0.57	91.93	3.05	0.401
9.02	9.25	7.06	1.24	82.44	3.11	0.406
11.00	11.03	7.06	3.05	56.80	4.59	0.540

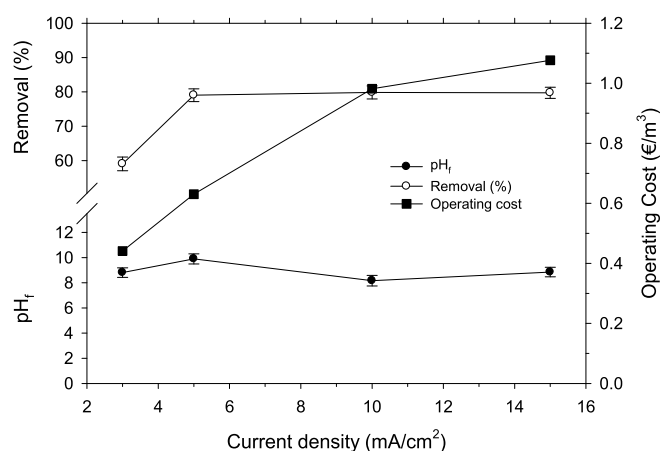
Current supply and voltage monitoring in the reactor was performed using a voltage source QPX1200SP (Aim-TTI, Huntingdon, United Kingdom). Either a maximum output voltage of 60 V or a maximum current of output of 50 A could be applied, both values subject to a maximum power of 1200 W. The entire device was controlled through a mini all-in-one PC (PiPO Technology Co., Shenzhen, China) equipped with Windows® and its own control software interface.

## 2.2. Procedures

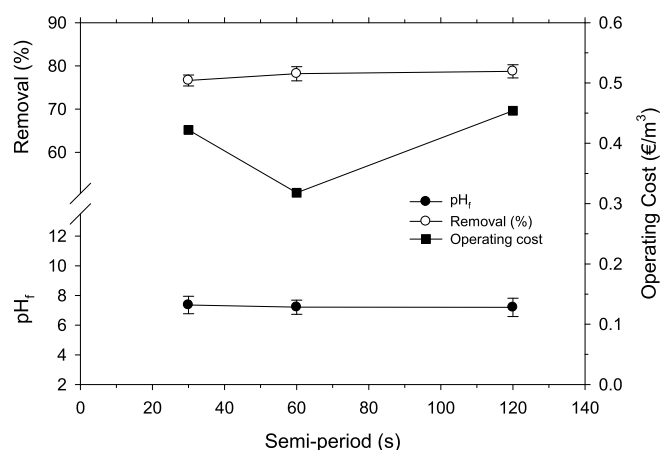
The effect of the operation parameters on the electrocoagulation process was investigated for the ranges listed in Table 2. The electrocoagulation tests were performed with groundwater from the Barranco



**Fig. 4.** Influence of the initial pH of the raw water on the performance of the EC reactor in batch operation. Operating conditions: initial  $F^-$  concentration, 7.06 mg/L; applied current density, 10 mA/cm<sup>2</sup>; run time, 30 min; distance between the aluminum electrodes, 5 mm. Error bars account for the standard deviation.



**Fig. 5.** Influence of the applied current density on the performance of the EC reactor in batch operation. Operating conditions: initial  $F^-$  concentration, 7.35 mg/L; initial pH, 8.75; run time, 30 min; distance between the aluminum electrodes, 5 mm. Error bars account for the standard deviation.



**Fig. 6.** Influence of the voltage change semi-period on the performance of the EC reactor in batch operation. Operating conditions: initial  $F^-$  concentration, 7.06 mg/L; initial pH, 7.16; run time, 600 min; distance between the aluminum electrodes, 5 mm. Error bars account for the standard deviation.

**Table 6**

Influence of initial pH and applied current density on the EC operation assuming pseudo first- and second-order kinetics. Operation conditions of the EC reactor: Operating time, 30 min; Current density, 5 mA/cm<sup>2</sup>; distance between the electrodes, 5 mm.

Parameter	Value	Pseudo first-order		Pseudo second-order	
		$k_1 (\times 10^2)$	$R^2$	$k_2 (\times 10^2)$	$R^2$
Raw water	30 min	4.30	0.9850	0.940	0.9883
pH	1	9.69	0.9579	6.75	0.7276
	3	13.16	0.9535	11.0	0.9581
	5	10.72	0.9553	7.15	0.9353
	7	9.33	0.8625	5.86	0.9023
	9	7.05	0.9751	2.51	0.8618
	11	2.72	0.5706	6.60	0.6255
Current density (mA/cm <sup>2</sup> )	3	4.09	0.9653	9.20	0.9874
	5	6.47	0.9185	2.35	0.9779
	10	6.74	0.8242	2.63	0.8960
	15	6.70	0.8786	2.56	0.9514

de Vergara Gallery located in La Guancha, Tenerife (see Fig. 1). The water was collected for transport to the laboratory without any previous treatment. The average chemical composition of the raw water is shown in Table 3. For all water collections, the fluoride concentration and the pH values were monitored before and at different stages of the electrocoagulation operation by potentiometry (Metrohm, Herisau, Switzerland). Fluoride analysis was performed using a fluoride ion-selective electrode connected to an 827 pH laboratory instrument equipped with an Ag/AgCl/KCl (saturated) reference electrode, while a 691 pH-Meter with an Aquatrode Plus combined pH electrode was employed for pH monitoring. A pH 5.5 buffer solution was added to the water samples to avoid interference from other ions on the ion-selective fluoride electrode. The system was calibrated using standard solutions of fluoride ion concentrations of 0.5–15 mg/L in distilled water. All chemicals used in the present experiment were of analytical grade.

The loss of Al at the anode was determined by weighing the electrodes prior and after the electrocoagulation process. In both cases, the electrode surface was subjected to a cleaning and conditioning process according to ASTM G1-03(2017)e1.

The percentage of fluoride removal was calculated using equation (1):

$$\text{Removal (\%)} = \frac{[F^-]_i - [F^-]_f}{[F^-]_i} \cdot 100 \quad (1)$$

where  $[F^-]_i$  and  $[F^-]_f$  are the initial and final concentration of fluorides in the solution, respectively.

A basic economic evaluation was carried out considering the costs of the electrode materials and the electricity consumed. The equation used for this cost estimate is:

$$\text{Operation Cost} = a \cdot EC_{\text{Electrode}} + b \cdot EC_{\text{Energy}} \quad (2)$$

where  $EC_{\text{Electrode}}$  is expressed as (kg Al lost)/m<sup>3</sup>, and  $EC_{\text{Energy}}$  as kWh/m<sup>3</sup> of treated water for the removal of fluorides. The parametric constants  $a$  and  $b$  were introduced to relate the costs to the Spanish market in 2018, amounting to 1.720 €/kg Al and 0.117 €/kWh, respectively. Analogously, the following equation was used to calculate the energy consumption:

$$\text{Energy consumption} \left( \frac{\text{kWh}}{\text{m}^3} \right) = \frac{\text{voltage} \cdot \text{current} \cdot \text{runtime}}{\text{working volume of reactor}} \quad (3)$$

In order to minimize scale formation on the surface of the aluminum electrodes that unavoidably accompany the dissolution reaction of the metal, the system was tested by applying DC current, although periodically alternating the polarity of the electrodes. In this way, half periods of polarity were applied to the electrodes that alternately operated as cathodes or anodes in the electrochemical cell. The half

periods considered in this investigation were 30, 60 and 120 s.

A kinetic characterization was conducted in order to establish the reaction order in the process. Although the reactions involved in the electrocoagulation process with aluminum electrodes are complex and are controlled by many variables that can affect each other, some information can be obtained from the tests. Therefore, it was considered that the process can be described by a pseudo-kinetic model in which the reaction rate is described by an  $n$ -th order mechanism as proposed by Thakur and Mondal (2017):

$$\frac{dC}{dt} = -k \cdot C^n \quad (4)$$

where  $C$  is the fluoride concentration,  $k$  is the kinetic constant,  $n$  is the reaction order, and  $t$  is the reaction time. Considering kinetics of pseudo-first and pseudo-second order, the integration of equation (4) leads to:

$$\text{Pseudo - first - order: } \ln \left( \frac{C_t}{C_i} \right) = -k_1 \cdot t \quad (5)$$

$$\text{Pseudo - second - order: } \frac{1}{C_t} - \frac{1}{C_i} = k_2 \cdot t \quad (6)$$

The kinetic constants can be determined from the values of the slope of the linear fits for each model.

The EC process was carried out under continuous flow cell conditions to evaluate the behavior of the system under operating conditions similar to those expected in pilot or real scales. Therefore, you must take into account any seasonal variation in the smallest and highest fluoride concentration of the natural groundwater. Accordingly, the residence time of the raw water to be treated inside the reactor was optimized, as well as the effect that the applied current density has on the efficiency of fluoride removal and the cost of operation. The residence time was established in 5, 8, 10 and 15 min by varying the water flow at the entrance of the electrochemical reactor.

### 3. Results and discussion

The optimization of the reactor and its subsequent validation to use this technique to treat natural groundwaters of volcanic origin was addressed in a previous work (Betancor-Abreu et al., 2019). In that work, the evolution of the mechanical design of the reactor using aluminum electrodes was explained in detail. We started with a reactor of 145 mL of capacity, formed by a system of two electrodes, which was converted into a reactor of 368 mL of capacity that contained a set of 4 electrodes (two anodes and two cathodes). Finally, we proceeded to the introduction of a set of multi-electrodes, increasing the volume of the reactor to 2000 mL, this being the optimal cell design employed for the tests performed in the present work. The configuration of this reactor consisted of a system of 14 aluminum electrodes separated by 5 mm as shown in Fig. 2.

Several tests were carried out to determine the influence of the current density, the pH, the duration of polarity change in the electrodes (half period), and the residence time of the sample in the reactor on the EC process. They were performed in batch mode and in steady state operation. Table 2 shows the ranges of variability of the parameters controlled and modified in the different optimization tests. These parameters were chosen due to their relevance in the process of fluoride removal using the electrocoagulation technique. All the tests were performed in triplicate to establish the reproducibility of the results.

#### 3.1. Batch tests

##### 3.1.1. Influence of the time of operation

The performance of the reactor was tested using four different operating times, namely 5, 8, 10 and 30 min. Table 4 shows the results



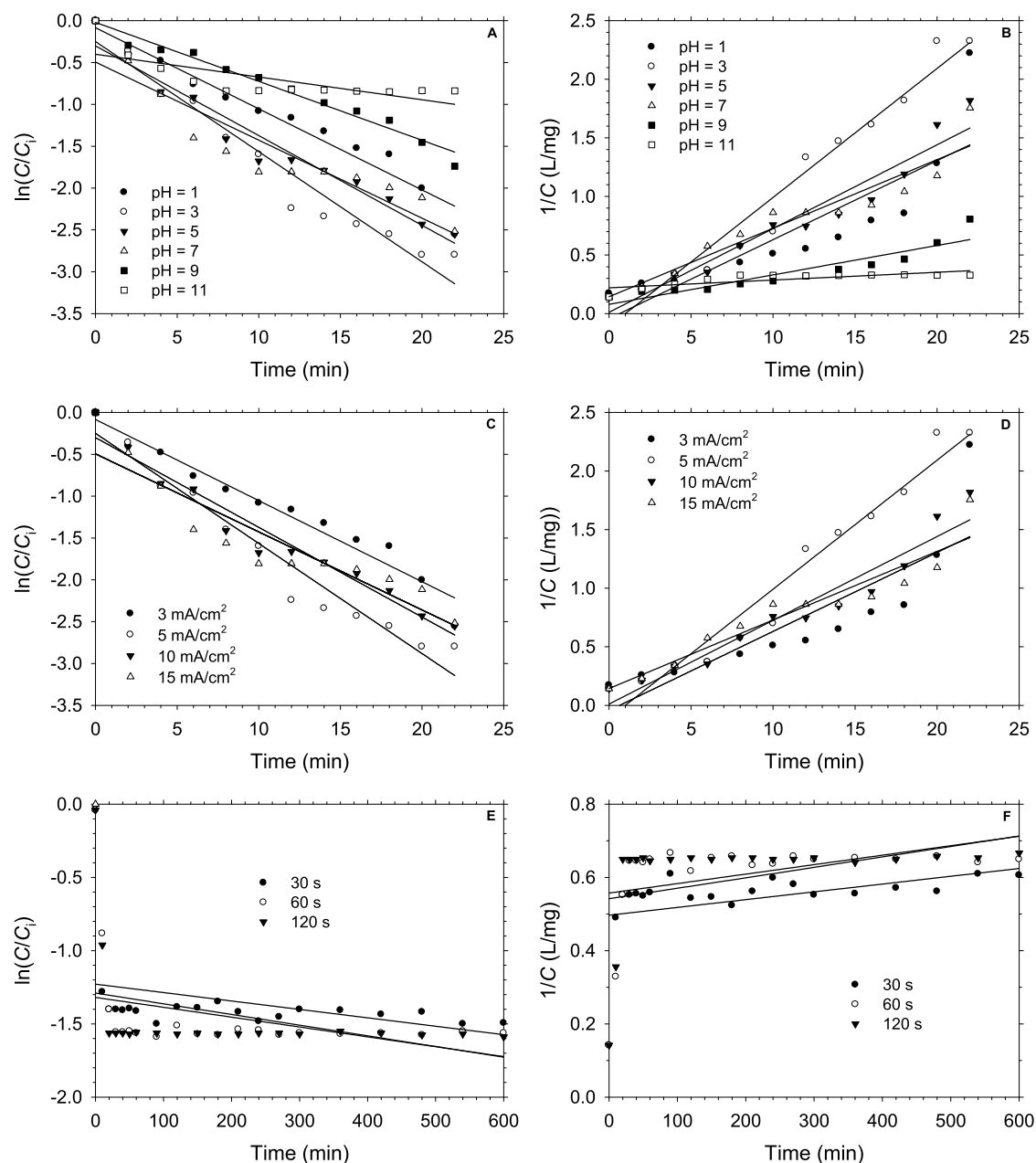


Fig. 7. Fits of average experimental data from batch tests to (A,C,E) pseudo-first- and (B,D,F) pseudo-second-order kinetic models. Effect of: (A,B) the initial pH; (C,D) the applied current density; and (E,F) the voltage change half period.

obtained in the tests, while Fig. 3 shows the experimental relationships found among the three parameters considered in this study. The percentage of fluoride removal was calculated according to equation (1).

When considering small operating times, a progressive reduction of the concentration of fluorides was observed. Thus, with 5 min of operation, fluoride elimination efficiencies higher than 68% were achieved, which increased up to 72% with 8 min, up to 78% with 10 min and, finally, up to almost 85% for operating times of 30 min. It is important to point out that obtaining final concentrations of fluorides within the established legal limits was only achieved for operating times longer than 30 min, although this was not the objective of the tests in this stage. In all cases there was an increase in the voltage drop of the system and a negligible pH change.

A preliminary economic evaluation was carried out considering the cost of the electrode materials and the electricity consumed according to equations (2) and (3). It was found that the operating costs in the

electrocoagulation operation show a power-law increase with respect to the treatment time (see Fig. 3A). A cost of 0.175 €/m<sup>3</sup> was determined for the water treated during 5 min, which increased to 0.278, 0.330 and 0.531 €/m<sup>3</sup> when the operating times were 8, 10 and 30 min, respectively. A similar trend was observed between the increase in the percentage of fluoride removal and the treatment time (cf. Fig. 3A). On the other hand, the dependence between operating costs and the percentage of fluoride removal is linear, as shown in Fig. 3B. This shows that for every 1% increase in fluoride removal, there is an estimated increase of 2 cents per cubic meter of water treated under the tested conditions.

### 3.1.2. Influence of initial pH

An important factor that influences the elimination of fluoride in the electrocoagulation operation is the pH of the raw water. It was reported that the pH of the solution can increase or decrease due to the reactions

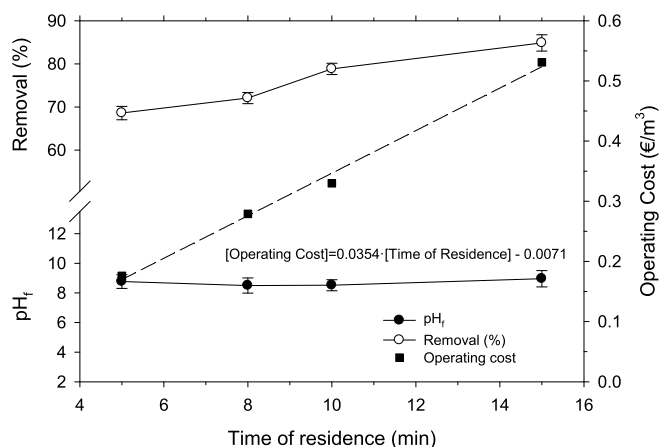
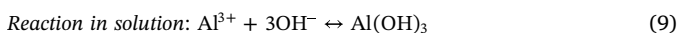
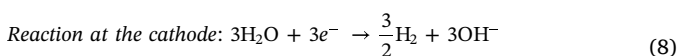
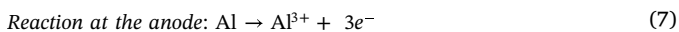


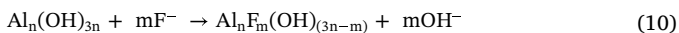
Fig. 8. Influence of the time of residence on the performance of the EC reactor under continuous-flow regime. Operating conditions: initial  $F^-$  concentration, 8.63 mg/L; initial pH, 7.30; run time, 110 min; distance between the aluminum electrodes, 5 mm. Error bars account for the standard deviation.

involved in the process, and that the direction of the pH change depends directly on the initial pH of the raw water, so that a final pH is reached within the range of 8–9.5 (Thakur and Mondal, 2017). Other studies have shown that the variation of the solution pH is smaller as the pH in the solution to be treated increases (Koby et al., 2003, 2006).

Therefore, to understand the impact of pH on the electrocoagulation process, we must take into account the processes involved. Equation (7) describes the dissolution process of aluminum at the anode, while reaction (8) refers to the reduction process that occurs in the cathode with the release of hydrogen gas and hydroxyl ions, which are responsible for the alkalization of the medium (Koby et al., 2011). The dissolved aluminum present in solution precipitates in the form of aluminum hydroxide as shown in equation (9), although this process is highly influenced by the pH.



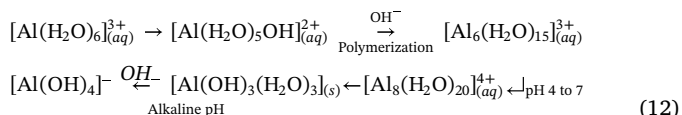
Although the scientific community has not yet established the exact mechanism for the process of fluoride removal by aluminum (Zhu et al., 2007), two alternative mechanisms are currently considered likely. They propose the elimination of fluoride by co-precipitation, as indicated in equation (10), or the removal of fluoride by adsorption given by equation (11):



In order to evaluate the influence on the electrocoagulation process due to the initial pH in the natural water, batch tests were performed with an operating time of 30 min. In these experiments, the initial pH was varied between 1 and 11 with intervals of 2 pH units. Table 5 and Fig. 4 summarize the results obtained. In general, it has always been observed that the pH of the medium shifted to more alkaline values, although its relative extent greatly varied from case to case. In this way, an increase of around 65% was observed in the case of pH 1, reaching a final value of pH 1.72. It can be seen that the change in pH follows an almost linear dependence with time ( $R^2 = 0.94$ ), and there is no accumulation of deposits at the bottom of the reactor. For the initial pH values 3 and 5, final pH values close to 5 were attained, while basic pH values were obtained for the remaining conditions considered. In all these cases, the formation of precipitates inside the reactor was

observed, which increased in quantity as the pH of the solution increased.

With respect to the percentage of fluoride elimination, it was greater than 90% in solutions with neutral or acidic pH values, and the maximum removal of fluorides was observed for water at pH 3. By contrast, the elimination efficiency decreased constantly as the medium became more alkaline. For example, although a fairly high removal percentage of 82.44% was still observed for the water with an initial pH of 9.02, the efficiency was abruptly reduced to 56.80% for pH 11. This characteristic can be explained by considering the different fluoride and aluminum ion species present in the solution as a function of pH. In summary, the pH-dependent polymerization reactions that may take place are the following (Rebhun and Lurie, 1993):



The pH range for the precipitation of aluminum hydroxide occurs between about 4 and 13. It is in this range that positively-charged aluminum polyhydroxide complexes are formed that act effectively as coagulants. These charged species can be transformed into  $\text{Al}(\text{OH})_3$  (s) (Behbahani et al., 2011), a compound of low solubility, which is finally polymerized as  $\text{Al}_n(\text{OH})_{3n}$ , leading to the formation of dense flocs. Therefore, the elimination of fluorides will be dominated, among other factors, by an attractive electrostatic interaction, which is directly influenced by the pH of the environment. At pH 3, the maximum fluoride removal was obtained, which confirms that electrostatic attraction prevails at this acid pH value. As the pH increases, the positive charge of colloidal particles of  $\text{Al}(\text{OH})_3$  is reduced, and the decrease was more abrupt at pH values higher than 9 due to the formation of  $\text{Al}(\text{OH})_4^-$ .

Finally, the operating costs will increase as the initial pH value increases. It was observed that for pH conditions between 7 and 9, which is the natural pH range of the treated water, the operating costs fluctuated around the same value, namely 0.40 €/m³ of treated water. Although the operating costs obtained in the range of pH 1–5 were somewhat lower, it should be borne in mind that the estimate of the cost was based solely on the energy consumption and the cost of the aluminum consumed, while the costs associated with the regulation of the pH were not considered at this stage.

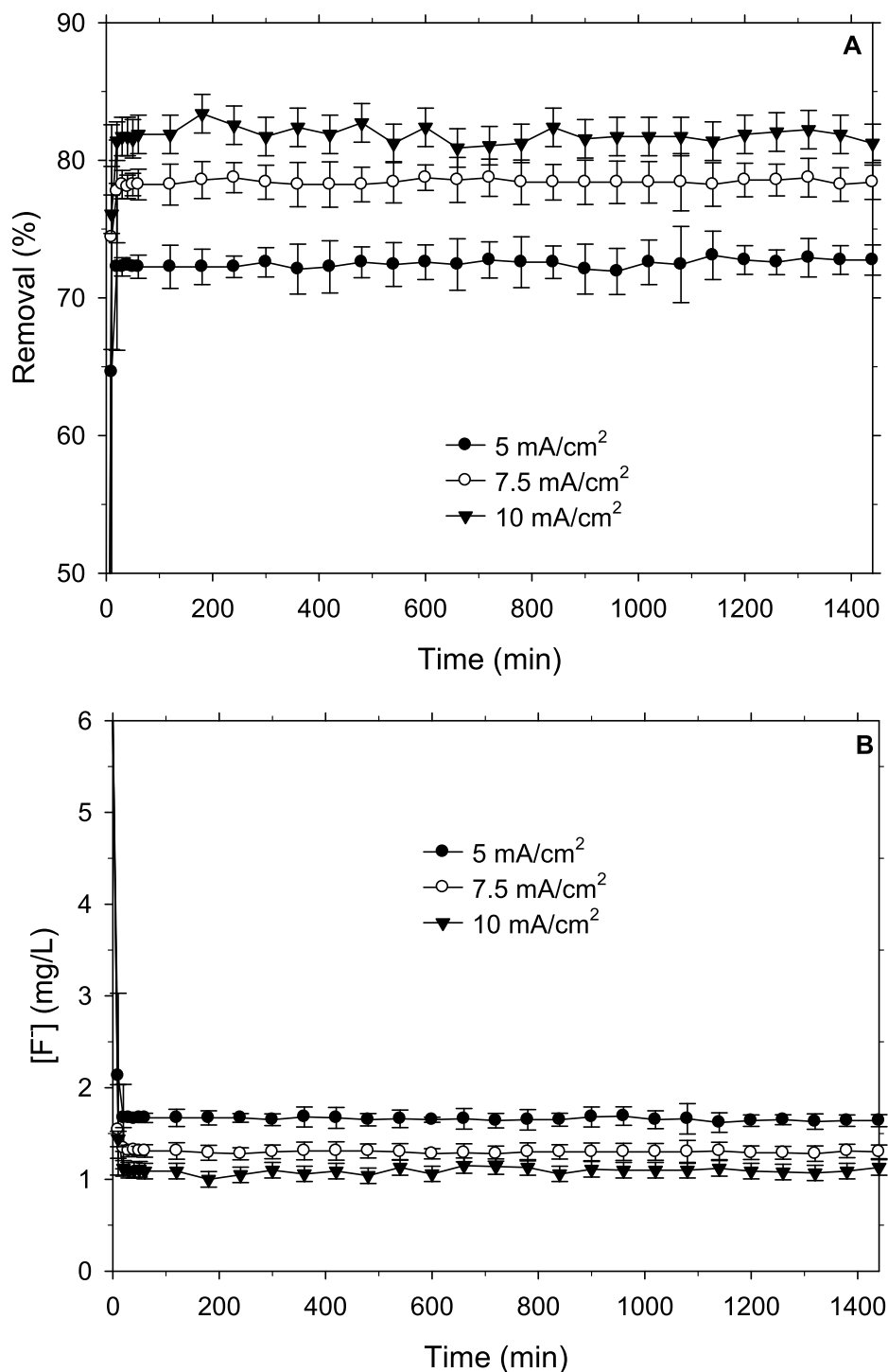
### 3.1.3. Influence of the current density

The formation and evolution of the flocs is directly related to the current density applied to the reactor. According to Faraday's law, the increase in the current flowing between the electrodes will lead to a larger coagulant production in the process. Fig. 5 shows the evolution of the percentage of fluoride removal, as well as the operating costs and pH, when the current density was varied in the range between 3 and 15 mA/cm². In general, the percentage of fluoride removal increased with the applied current density, reaching a maximum of about 80% elimination. For current densities greater than 3 mA/cm², values close to 80% elimination were already obtained, while the associated operating costs increased linearly with the current density ( $R^2 = 0.9801$ ). By considering only the influence of current density and, therefore, by not assessing other variables that may be involved in the removal of fluorides and the cost of operation, an optimum condition between 5 and 10 mA/cm² was established.

### 3.1.4. Influence of voltage reversal

Fig. 6 summarizes the results obtained by changing the duration of the polarization half period. It is clearly observed how the half period has a greater effect on operating costs than on the efficiency of fluoride removal. Therefore, the percentage of fluoride removal increased as the half period increased, albeit with very modest increments ranging from 76.63% for a half period of 30 s–78.75% for a half period of 120 s (i.e.,





**Fig. 9.** Performance of the EC reactor in continuous-flow operation for a water sample with 6.02 mg/L initial fluoride concentration. (A) At the beginning of the test, and (B) after 24 h operation. Operating conditions: initial pH, 8.41; current density, 10 mA/cm<sup>2</sup>; time of residence, 10 min; distance between the aluminum electrodes, 5 mm. Error bars account for the standard deviation.

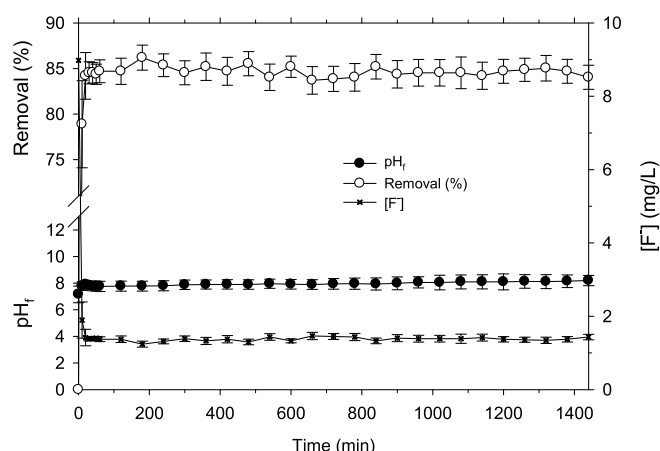
an increase of approximately 2.8%). On the contrary, operation costs decreased for a half period of 60 s, which seems to indicate that at this alternating cathode/anode frequency there was smaller blockage of the electrode surface by scaling and, therefore, effectively favored the dissolution of aluminum.

### 3.1.5. Kinetic characterization

The main objective of the kinetic characterization was to establish the reaction order in the process. Although the reactions involved in the

electrocoagulation process with aluminum electrodes are complex and are controlled by many variables that can affect each other, some information can be obtained from the tests described in the previous sections.

In this study, we have evaluated the degree of adjustment of our data considering the sample of untreated water and, subsequently, evaluating the effects caused varying both the initial pH and the applied current density. Table 6 summarizes the results obtained using this procedure, whereas Fig. 7 depicts the plots containing the fitted data to



**Fig. 10.** Performance of the EC reactor after 24 h operation in continuous-flow regime for a water sample with 8.98 mg/L initial fluoride concentration. Operating conditions: initial pH, 7.16; current density, 10 mA/cm<sup>2</sup>; time of residence, 10 min; distance between the aluminum electrodes, 5 mm. Error bars account for the standard deviation.

**Table 7**

Compliance of the product water to the legal requirements.

Parameters	Legal requirement	Average values in the product water	
		[F <sup>-</sup> ] <sub>i</sub> = 6.02 mg/L	[F <sup>-</sup> ] <sub>i</sub> = 8.98 mg/L
Current density	–	7.5 mA/cm <sup>2</sup>	10 mA/cm <sup>2</sup>
Fluoride	1.5 mg/L	2.2 mg/L	1.30 mg/L
Aluminum	200 µg/L	50 µg/L	50 µg/L
pH	6.5–9.5	9.10	8.20

the models. When applying the kinetic models to describe the treatment of the raw water, it is observed that even during a test time of 30 min the obtained data were adjusted to a similar level of precision in both kinetic models, although slightly better with the second-order pseudo-kinetic model.

In experiments varying the initial pH of the solution and fitting the kinetics described by equations (5) and (6), it was observed that both models satisfactorily fit the experimental data, independently of pH, with the exception of pH 11. In this case, significant deviations were observed between the simulated and experimental data for both models, that is,  $R^2 = 0.5706$  for the pseudo-first-order kinetics and  $R^2 = 0.6255$  for the pseudo-second-order kinetics. This feature may be due to the interference produced by the formation of  $\text{Al}(\text{OH})_4^-$  on the adsorption and attraction of fluoride ions to the alumina flocs.

Likewise, the kinetics of the EC process was evaluated with respect to the variation of the applied current density. It was observed that the fits to the proposed models worsened for a current density of 10 mA/cm<sup>2</sup>, while they improved for higher current densities.

### 3.2. Continuous flow regime

Based on the results previously obtained considering a discontinuous regime, the EC process was next carried out under continuous flow cell conditions to evaluate the behavior of the system under operating conditions similar to those expected in pilot or real scales. The residence time of the raw water to be treated inside the reactor was optimized, as well as the effect that the applied current density has on the efficiency of fluoride removal and the cost of operation.

#### 3.2.1. Influence of residence time

The residence time was established in 5, 8, 10 and 15 min by

varying the water flow at the entrance of the electrochemical reactor. The percentage of fluoride removal, pH variation and the operating costs of the process were analyzed as shown in Fig. 8. It was found that operating costs increased with the increase of residence time. Thus, for an increase in residence time from 5 to 15 min, operating costs increased by approximately 203%. The percentage of fluoride elimination also increased in a longer residence time, leading to a maximum elimination of 85% for a residence time of 15 min, almost without variation in the pH of the medium.

On the other hand, the variation of the operating costs with the residence time followed a linear trend with a fit quality of  $R^2 = 0.9946$ , finding that the operating cost increased 0.035 € for each minute that increases the residence time.

#### 3.2.2. Influence of the current density during long-duration tests

The current density exerts a determining effect on the amount of fluoride removed, given the electrochemical nature of the process. From what was observed in the previous tests, the applied current density will depend, for a fixed residence time, on the initial concentration of fluoride present in the raw water. Based on the results obtained in the previous section, a residence time of 10 min was established and the effect of the current density was analyzed when treating two raw waters that had the minimum and maximum fluoride concentrations registered during the entire study period. The aim was to observe the effect of the variation in the fluoride concentration and the pH of a real sample due to the variations in the quality of the raw water due to seasonal effects. The first sample had an initial fluoride concentration of 6.02 mg/L and a pH of 8.41, while the second sample had an initial fluoride concentration of 8.98 mg/L and a pH of 7.16.

**3.2.2.1. Raw water with fluoride concentration of 6.02 mg/L.** Fig. 9A–B shows the evolution of fluoride concentration and the percentage of fluoride removal over time for a 24-h test by applying to the system current densities of 5, 7.5 and 10 mA/cm<sup>2</sup>. For the three current densities, a drastic decrease in the concentration of fluorides was observed in the first minutes of operation. Thus, there was a reduction in fluoride concentration greater than 64% in the first 10 min, increasing to 72.8% at 24 h, which was recorded for a current density of 5 mA/cm<sup>2</sup>; this was an operating condition that exhibited the poorest removal efficiencies at all times. Even then, this elimination rate corresponds to a final fluoride concentration of 1.64 mg/L. In general, it was observed that fluoride elimination occurred significantly during the first 20 min of testing, with values of 1.67 mg/L that would vary very little throughout the remaining duration of the test, with an average of 1.66 mg/L. Next, for a current density of 7.5 mA/cm<sup>2</sup>, the elimination rate increased to 74.4% in the first 10 min, then stabilized to 78.4% after 24 h. The corresponding fluoride concentrations were 1.34 mg/L at 20 min, and 1.30 mg/L at the end of the test. On average, the composition throughout the complete test was 1.30 mg/L, always below the maximum legal requirement. Furthermore, for a current density of 10 mA/cm<sup>2</sup>, the same trend was observed as in the previous two cases, resulting in a final fluoride concentration of 1.13 mg/L, which represents an elimination percentage of 81.2%, and an average of 1.09 mg/L that was already reached after 20 min of operation. In addition, a linear dependence was found between the percentage of fluoride removal and the applied current density. Thus, for each 1 mA/cm<sup>2</sup> increase in the current density, the percentage of fluoride removal increased by 1.7%. In these cases, the energy consumption was of an order of similar magnitude, 1.7 kWh/m<sup>3</sup> for a current density of 7.5 mA/cm<sup>2</sup> and 1.9 kWh/m<sup>3</sup> for a current density of 10 mA/cm<sup>2</sup>. Operating costs varied within a very small range, namely between 0.20 and 0.22 €/m<sup>3</sup> of treated water.

In all cases there was alkalization of the medium over time and with the increase of the applied current density. Thus, a final pH of 8.9 occurred at 24 h for a current density of 5 mA/cm<sup>2</sup>, while the pH

increased to 9.1 and 9.65 for the current densities of 7.5 and 10 mA/cm<sup>2</sup>, respectively. A visual inspection of the aluminum electrodes evidenced increased scale formation on the surface of the electrodes, which may account for a decrease in the percentage of fluoride reduction in the water. These scales reduce the electrode/solution contact area, which, for long periods of work, may result in a loss of fluoride removal performance or in the need to increase the energy supplied to the system.

**3.2.2.2. Raw water with fluoride concentration of 8.98 mg/L.** In the case of raw water with an initial fluoride concentration of 8.98 mg/L, it was observed that the final concentration of fluoride after 24 h of operation decreased to 2.25 and 1.91 mg/L when applying current densities of 5 and 7.5 mA/cm<sup>2</sup>, respectively, values higher than the maximum allowed by legislation in force. The increase in current density to 10 mA/cm<sup>2</sup> resulted in a decrease in the fluoride concentration to 1.42 mg/L after 20 min of operation, and subsequently oscillated between 1.24 and 1.46 mg/L for the remaining 24-h test. The final fluoride concentration was 1.43 mg/L after 24 h, and the average content in the treated water was 1.38 mg/L. Fig. 10 shows the evolution of fluoride concentration as function of pH and the percentage of fluoride removal over time. An alkalization of the medium was also observed, since the pH increased from an initial value of 7.11 to a final value of around 8.5. Regarding operating costs, it was found that, for a work regime of 24 h, the associated cost was 0.261 €/m<sup>3</sup> of treated water.

Bearing in mind that the main objective of this study was focused on the treatment of groundwater that will be used in water supply networks for human consumption, it is expected to comply with the most restrictive regulations currently in force in Spain (Real Decreto 140, 2003). For comparative purposes, Table 7 shows the highest legal allowances established for the main parameters of water, as well as those obtained in the 24-h continuous tests performed using current densities that allowed to obtain fluoride concentrations below the established legal limits. It is readily observable that both the pH and the fluoride concentration in the product water met the ranges allowed for these parameters during testing. In addition, when the raw water was tested with a variability in the concentration of fluorides and the pH around the limit values listed in Table 3, this implied that the applied current density had to be adjusted according to the initial concentration of fluorides. In any case, operating costs did not increase substantially during this operation.

Finally, compared to the operating cost of reverse osmosis, which varies between 0.56 and 0.63 €/m<sup>3</sup> of treated water for processes up to 140,000 m<sup>3</sup>/day, as in our case (Martínez Vicente, 2002), electrocoagulation seems to be more economic process for the previous treatment of water. Moreover, compared to electrodialysis, which presents treatment costs between 0.35 and 0.45 €/m<sup>3</sup> of treated water (Martínez Vicente, 2002), although the costs are similar, the electrocoagulation process does not present water flow losses, which means it can be implemented as pretreatment of groundwater before a general treatment by electrodialysis.

#### 4. Conclusions

Electrocoagulation is presented here as an efficient method to remove fluorides from groundwater of volcanic origin. The operating conditions have been optimized both in batch and continuous-flow operation regimes for a 2 L capacity reactor composed of 14 aluminum electrodes of dimensions 5 cm × 12 cm, with a separation of 5 mm between them.

The use of the EC technique for the treatment of natural waters was validated through the tests carried out in the batch regime. With respect to the natural pH of the water, it was found that the previous acidification of the water improved the efficiency of fluoride removal, with an optimum condition for pH 3. In this case, a fluoride removal up to

93.91% was attained leading to a fluoride concentration of 0.43 mg/L in the product water and operating costs of 0.318 €/m<sup>3</sup> of treated water. The percentage of fluoride removal varied between 68.9 and 84.7% for operating times that ranged from 5 to 30 min. As for the current density, an optimum was found for 5 mA/cm<sup>2</sup> based on the percentage of fluoride removal. The kinetics of fluoride removal was adjusted to a pseudo-second order law when investigating the influence of both the initial pH and the applied current density.

The optimal operating conditions found for the continuous-flow operation of natural groundwater without previous conditioning were established considering the initial concentration of fluoride. Therefore, for the range of variability of the fluoride concentration found during the analysis period, the optimal current densities ranged between 7.5 and 10 mA/cm<sup>2</sup> for waters with fluoride concentrations varying between 6 and 9 mg/L, establishing a residence time of 10 min.

The final concentration of fluoride in the treated water was below the established legal limit of 1.5 mg/L according to WHO guidelines for all the configurations employed in this work, and the operating costs ranged between 0.20 and 0.26 €/m<sup>3</sup> of treated water.

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