



Fluoride removal from synthetic groundwater by electrocoagulation process: parametric and energy evaluation

Amel Chibani^a, Afef Barhoumi^a, Sana Ncib^a, Wided Bouguerra^{a,b,*}, Elimam Elaloui^a

^aUR Materials, Environment and Energy, Faculty of Science of Gafsa, University of Gafsa, Campus Sidi Ahmed Zarroug, Gafsa 2112, Tunisia, emails: bg_wided@yahoo.fr (W. Bouguerra), amel_chibani1989@yahoo.fr (A. Chibani), afefbarhoumi@yahoo.fr (A. Barhoumi), sana_ncib@yahoo.fr (S. Ncib), limam_aloui@yahoo.fr (E. Elaloui)

^bCommon Services Unit for the Research, Faculty of Science of Gafsa, University of Gafsa, Campus Sidi Ahmed Zarroug, Gafsa 2112, Tunisia

Received 24 April 2018; Accepted 10 March 2019

ABSTRACT

This study investigates the effect of several parameters on the electrocoagulation process has been studied in order to optimize the evolution of the fluoride removal percentage and the energy consumption. Optimum experimental conditions of fluoride removal were determined as: $\text{pH}_i = 6$, $J = 0.27 \text{ mA/cm}^2$, $t_{\text{EC}} = 30 \text{ min}$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $d_i = 1 \text{ cm}$, $S/V = 7.2 \text{ m}^{-1}$ and Stirring speed = 300 rpm with two aluminum electrodes. These operating conditions are allowed to achieve fluoride removal of over 85% in a relatively short operating time with low energy consumption (0.0396 kWh/m³). The results fitted with the Langmuir and Freundlich equations showed that fluoride removal was achieved by a monolayer adsorption, with a finite number of identical sites. To study the rate-limiting step, the kinetic data of fluoride were analyzed using first-order and second-order kinetic models. Under optimal conditions with 10 and 20 min treatment, fluoride was completely removed for initial concentration of 3 and 6 mg/L respectively. Moreover, for fluoride initial concentration of 10 mg/L, it is possible to reach a residual concentration under the limit recommended by WHO for fluoride concentration in drinking water (1.5 mg/L) with lowest consumption of electricity.

Keywords: Drinking water; Fluoride removal; Aluminum electrode; Electrocoagulation; Energy consumption; Kinetic study; Adsorption isotherm

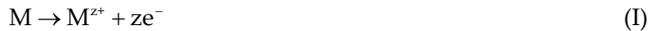
1. Introduction

Drinking water is the main source of fluoride intake. Fluoride concentrations, as a component in natural sources of drinking water, generally vary from 1 to 10 mg/L in the phosphate zones [1,2]. An excess intake of fluoride can lead to various diseases such as osteoporosis, thyroid disorder, neurological damage, mottling of teeth, and fluorosis of skeleton, cancer, infertility in women, Alzheimer's syndrome [3–5]. To prevent these harmful consequences, especially problems resulting from fluorosis that harms bones and teeth, the World Health Organization (WHO) fixed the maximum acceptable concentration of fluoride anions in drinking water to 1.5 mg/L [6].

In the recent decades, different techniques have been used to remove fluoride from contaminated drinking water such as adsorption, chemical coagulation, membrane separation and electrocoagulation (EC) [7–9].

Electrochemical technology contributes in many ways to a cleaner environment and covers a very broad range of technology [10–12]. Electrocoagulation process is one of the electrochemical methods that have been developed for drinking water treatment. EC is based on producing, in situ, metal ions by progressive dissolution of the sacrificial anode of an electrochemical cell receptor under the effect of an electric current there through. This cell denoted by “electrocoagulator” contains in its simplest configuration two metal electrodes generally identical. The oxidation half-reaction causes the dissolution of the anode according to the electrochemical reaction (I):

* Corresponding author.



By combining with the OH^{-} ions from the cathodic reduction of water (II):



The metal cations generated at the anode lead to various complexes (hydroxo-metal species) which act as coagulant and promote the formation of flocs by destabilization of the polluting matter and suspended particles [13]. According to their densities, the flocs can settle before being filtered, or can float as a result of the hydrogen micro-bubbles produced at the cathode; in the case of electrocoagulation-electroflotation. Most applications use iron or aluminum electrodes because of their low cost and high valencies of the cations they generate. Aluminium was reported to be very effective and successful in fluoride removal.

Depending on pH, Al^{3+} and OH^{-} ions generated by electrode reactions react to form various monomeric species such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^{+}$, $\text{Al}(\text{OH})_3$ and polymeric species, such as $\text{Al}_6(\text{OH})_{15}^{3+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_8(\text{OH})_{20}^{4+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ and $\text{Al}_{13}(\text{OH})_{34}^{5+}$, which are transformed mostly into $\text{Al}(\text{OH})_3$ according to complex precipitation kinetics. $\text{Al}(\text{OH})_3$ has a strong affinity to adsorb fluoride [14]. Several studies have demonstrated that EC process using sacrificial electrodes is an efficient process for fluoride removal [15–20].

The aim of this work is to reduce the excess of fluoride in water by electrocoagulation by optimizing experimental conditions. The effect of initial pH, current density, initial fluoride concentration, electrolyte doses, the inter-electrode distance, stirring speed, the number of pair of electrodes, the connection mode and energy consumption were studied.

2. Materials and methods

2.1. Materials

Desired concentrations of fluoride solution were obtained by adding proper amount of sodium fluoride into distilled water. The conductivity of the sample water was varied by adding sodium chloride (NaCl).

2.2. Analytical methods

The pH was measured by a pH meter (CyberScan pH 510, WDW, Germany), which was freshly calibrated before each test.

The conductivity of the samples was determined by a conductimeter (Jenway 4510, Metrohm).

The fluoride concentration was determined by ion chromatography (IC) method (Metrohm 850 Professional IC). IC is selective, sensitive and fast method of anion content determination in water. This method enables direct determination of anions in water on the level of $10^{-6}\%$ to $10^{-4}\%$, depending on anion, sample volume and instrument [21].

2.3. Electrocoagulation test

EC cell consists of a cylindrical beaker with capacity of 1 L of volume, with a wooden cover to support the whole parallel aluminum plates used as sacrificial electrodes.

The electrodes used in this study were formed by two parallel rectangular aluminum plates ($25\text{ cm} \times 8\text{ cm} \times 0.2\text{ cm}$). Only one side of each electrode was taken as working surface; the inactive area of the electrodes was wrapped with tape and sustainable water resistant to fix the submerged area and avoid the loss of anode. The electrodes assembly was connected to DC power supply (AFX 2930 SB DC power supply 0–30 V/0–3 A dual output, 5 V to 3 A fixed output, part number: 9660 SB, AFX) providing current and voltage in the range of (0–10 A) and (0–30 V). The anode-cathode distance varies according to the experiment. The tests were performed at a varied magnetic stirring speed.

The electrodes were cleaned before each test by treating them with NaOH (2 M) and HCl (2 M) aqueous solutions after mechanically polishing underwater with abrasive paper [10,12]. The initial pH of the solutions was adjusted by adding either HCl (0.1 M) or NaOH (0.1 M) and NaCl as supporting electrolyte. For each experiment, the residual fluoride in the sample was filtered through filter paper (Millipore) and determined. The percentage of fluoride removed (%R) is given by the following equation:

$$\%R = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f were the initial and residual concentration of fluoride in the solution (mg/L).

3. Results and discussions

3.1. Effect of electrolysis time

The duration of electrolysis is one of the important parameters in the defluorination process by electrocoagulation [22].

The representative curve (Fig. 1) shows a very rapid increase in percentage of elimination within the first 15 min to 66.88%. Beyond 30 min, fluoride removal becomes constant with time and reaches 90%. These results are verified on the basis of the Faraday law. The amount of aluminum generated depends on electrolysis time [23].

The energy consumption (EC) is evaluated by the following equation:

$$EC = \frac{U \times I \times t}{V} \quad (2)$$

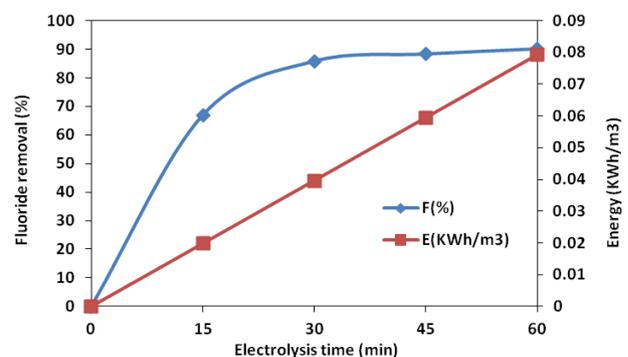


Fig. 1. Evolution of fluoride removal and energy consumption as a function of electrolysis time ($J = 0.27\text{ mA/cm}^2$; $\text{pH}_i = 6$; $[\text{NaCl}] = 0.5\text{ g/L}$; $C_i = 10\text{ mg/L}$; $d_i = 1\text{ cm}$).

where EC: Energy consumption in kWh/m³; U: Voltage in V; I: current imposed in A; T: Electrolysis time in h; V: Volume of the solution in m³.

Theoretically, the energy consumption depends on electrolysis time: the increase in electrolysis time leads to energy consumption increase. In this case, the values varied from 0.0078 to 0.0792 kWh/m³ for 5 and 60 min. The fluoride removal percentage is not significant for an electrolysis time exceeding 30 min. Thus, 30 min of electrolysis make it possible to reach the desired goal with energy consumption of 0.0396 kWh/m³.

When the electrolysis time is increased, the dissolved aluminum increases and promotes the formation of adsorbing coagulant of fluorides in solution [24]. So it is beneficial to raise the treatment time to achieve an effective elimination of fluoride. Nevertheless, this increase in time stimulates the loss of the electrodes [25]. To make our process more economical and cost-effective, it is sufficient to limit the electrolysis time to 30 min.

3.2. Effect of initial pH

The pH is an important parameter that influences the fluoride removal by EC process. To study the effect of initial pH (pH_i) on fluoride removal, a series of experiments was carried out at different pH_i (4, 5, 6, 7, 8 and 10) for an initial fluoride concentration (C_i) equal to 10 mg/L, a current density (J) equal to 0.27 mA/cm² with 0.5 g/L NaCl for an electrolysis time of 30 min and distance inter-electrodes equal to 1 cm. The pH of the solution, adjusted initially, is controlled throughout the duration of electrolysis.

As observed in Fig. 2, at pH6, the kinetic of fluoride removal is the most important close to 50%. EC is highly dependent on solution pH. It is linked to the aluminum diagram speciation, promoting the hydroxide species formation and flocs presence [26]. At less acidic pHs, more efficient removal is observed. It is linked to the presence of the aluminum hydroxide form (Al(OH)²⁺ and Al(OH)₂⁺) and thus the favored formation of the fluoroaluminium complexes. It is also possible to distinguish, from the solubility diagram of Al(OH)₃, the predominance of aluminum hydroxides in the vicinity of neutrality [27,28]. Defluorination is less favorable in the formation of Al(OH)₄⁻ soluble (pH = 10) as well as the

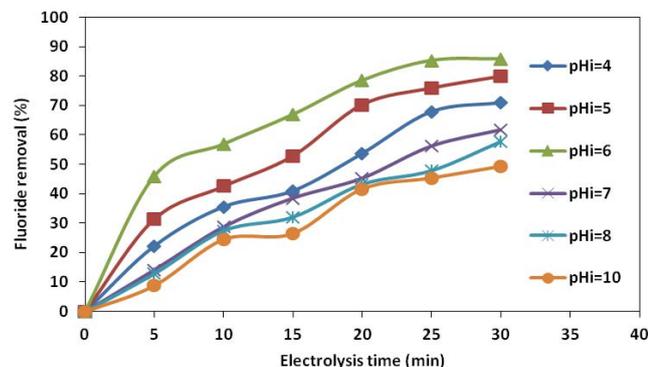
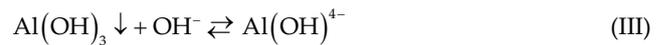


Fig. 2. Effect of the initial pH on fluoride removal as a function of electrolysis time (J = 0.27 mA/cm²; [NaCl] = 0.5 g/L; C_i = 10 mg/L; d_i = 1 cm).

formation of flocs [29]. The choice of pH_i of 6 as optimum is attributed to the existence of different complexes in fluoride aqueous solutions as shown in Fig. 3.

As observed in Fig. 4, the pH of the acidic solutions increases and tends towards 8 over time. The pH increase verifies the release of the hydroxide ions during the electrolysis process [30]. For pH_i greater than 8 the treated solution pH decreases slightly to stabilize at values near to 8 under the effect of the system Al(OH)₃/Al(OH)₄⁻ [31]. This decrease in pH is explained by reaction between OH⁻ and aluminum hydroxides Al(OH)₃.



The evolution of the pH of the solution depends on kinetics of the production of the hydroxide ions (OH⁻) or the (H⁺) protons. As a result, the optimal pH_i is chosen to be 6.

3.3. Effect of current density

The current density is a critical parameter of electrochemical process. It is directly linked to the imposed current and the active surface of the electrodes used. It controls the kinetics of the anodic oxidation reaction and that of the production of hydrogen bubbles at the cathodes [32]. It determines not only the dosage coagulant level, but also the rate of bubble production, size and growth of the floc, which may affect the efficiency of electrocoagulation [33]. The evolution of the

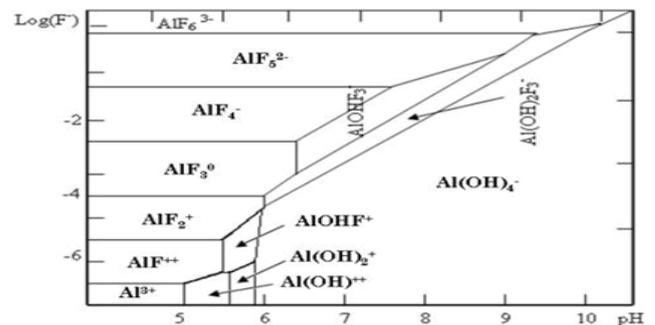


Fig. 3. Predominance of hydroxofluoroaluminium complexes.

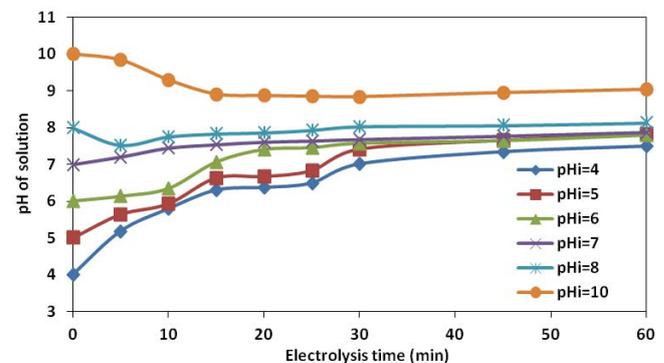


Fig. 4. Evolution of the pH as a function of electrolysis time (J = 0.27 mA/cm², [NaCl] = 0.5 g/L, C_i = 10 mg/L, d_i = 1 cm).

electrolysis time required is inversely proportional to that of the current density [34]. Studying the influence of current density on the fluoride removal process, a series of experiments is performed at different current intensities ranging from 10 to 100 mA (from 0.13 to 1.38 mA/cm²).

As shown in Fig. 5, the increase in the density of the current stimulates the dissolution of the anode, which in turn increases the amount of the coagulant [33]. The Faraday law can be used to explain the ratio of the current density, the electrolysis time and the amount of dissolved aluminum.

In fact, a high current density leads to a good removal of fluorides in water. More than 90% has been removed in 30 min. The reduction kinetics of the water at the cathode increases as a function of the current density. However, the amount of hydrogen formed increases and their sizes decrease, which is favorable for a good elimination by flotation [34]. In addition, it increases the release of the hydroxide ions and therefore the pH of the solution (Fig. 6). On the other hand, it should be noted that a higher current density increases the consumption of electrodes and energy (Table 1) [25,33].

According to Table 1, the abatement of fluoride in water, as a function of the applied current density, varies from 50.72 to 90.3% with respective energy consumptions of 0.0198 and 0.288 KWh/m³ when the current density varies from 0.13 to 1.38 mA/cm². The removal efficiency is beneficial from

Table 1

Effect of current density on fluoride removal and energy consumption (pH_i = 6, [NaCl] = 0.5 g/L, C_i = 10 mg/L, d_i = 1 cm)

Current density J (mA/cm ²)	Fluoride removal (%)	E (KWh/m ³)
0.13	50.72	0.0198
0.27	85.76	0.0396
0.55	85.52	0.0936
0.83	88.03	0.1728
1.11	88.94	0.2304
1.38	90.3	0.288

a current density of 0.27 mA/cm² (85.76%). we concluded that a low current density is sufficient to treat a water containing initially 10 mg/L of fluorine for 30 min with low energy consumption.

3.4. Effect of the amount of added salt

The addition of an electrolyte increases the electrical conductivity of the medium and reduces its resistance to ensure better dissolution of the anodes and to avoid the formation of an insulating layer on the surface of the electrodes and thus increase the resistance of the electrochemical cell. The comparison between salts such as NaCl and Na₂SO₄ showed that NaCl is the most effective carrier electrolyte for EC [35,36]. Chloride ions significantly reduce the negative effects of other coexisting ions such as CO₃⁻ and SO₄²⁻, which can form an insulating layer on the electrode surface and increase the resistance of the electrochemical cell [37]. In order to determine the effect of the salinity of the medium on the efficiency of the electrocoagulation to remove fluoride, we carried out EC tests under the same conditions and changed each time the amount of NaCl added varying from 0.1 to 0.7 g/L.

The evolution of the Fluorine removal is correlative with the quantities of the NaCl added (Fig. 7). The highest fluorine removal is obtained starting from 0.5 g/L of NaCl. This result is in agreement with the literature; It can be explained by the phenomenon of corrosion and oxidation under the effect of chloride ions on the electrodes which induce the formation of the flocs and inhibit the formation of a passive film on the surface [36,38].

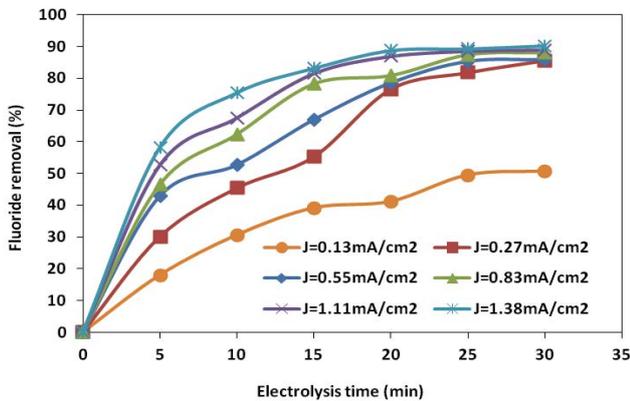


Fig. 5. Effect of current density on fluoride percent removal as a function of electrolysis time (pH_i = 6, [NaCl] = 0.5 g/L, C_i = 10 mg/L, d_i = 1 cm).

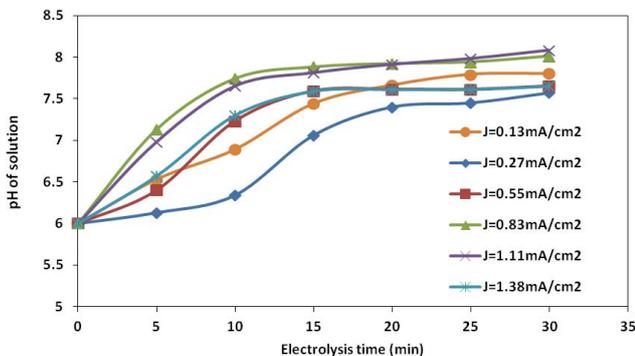


Fig. 6. Evolution of pH as a function of electrolysis time (pH_i = 6, [NaCl] = 0.5 g/L, C_i = 10 mg/L, d_i = 1 cm).

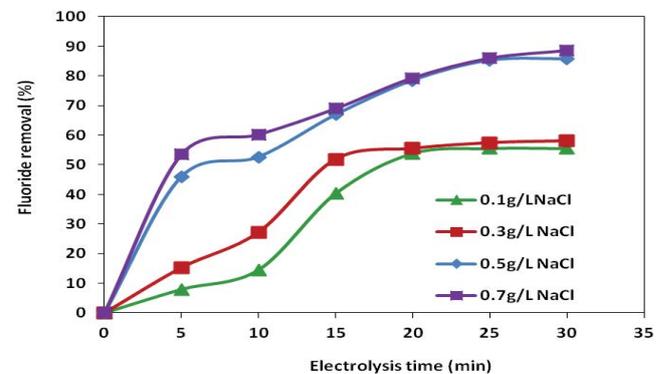
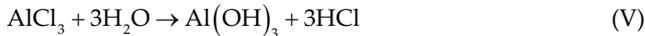


Fig. 7. Effect of NaCl concentration on the percentage of elimination as a function of electrolysis time (pH_i = 6, J = 0.27 mA/cm², C_i = 10 mg/L, d_i = 1 cm).

The corrosion phenomenon is summarized in the following reactions:



The addition of NaCl increases the flow of current in the EC cell, which leads to an overconsumption of the electrodes under the effect of undesirable corrosion [39]. Q. Zuo and coworkers reported that as the chloride concentration increased, defluorination was inhibited slightly. In case of high NaCl concentration (1 and 1.5 g/L), removal of fluoride reduces. The positive role could be offset by the negative role, and therefore, chloride had only little effect on the defluorination [40].

It is therefore beneficial to choose a small amount of NaCl to be added for efficient elimination and low consumption of the electrodes. In our case, we choose 0.5 g/L of NaCl as support electrolyte.

3.5. Effect of initial concentration

In southern Tunisia, fluoride content in natural waters is around 4 mg/L and can reach up to 10, which exceeds the WHO standard (1.5 mg/L) [1,41]. We have broadened the range of fluorine concentrations somewhat in our tests. In order to study the influence of initial fluoride concentration on EC, initial concentrations tested were: 3, 6, 10 and 12 mg/L, whereas the other parameters, initial pH, current density and NaCl concentration, were fixed. Fig. 8 represents the effect of initial concentrations on defluorination rate by electrocoagulation.

The kinetics of electrocoagulation decreases with the increase in the initial concentration. For low initial concentration, the elimination was more rapid and efficient. The standard limit is reached by the first 10 min of electrolysis for initial concentration equal to 3 mg/L. While, standard limit is not reached for 12 mg/L until up to 30 min (Table 2).

3.6. Effect of inter-electrode distance

The inter-electrode distance is an indispensable parameter in the electrocoagulation process. It is useful to highlight

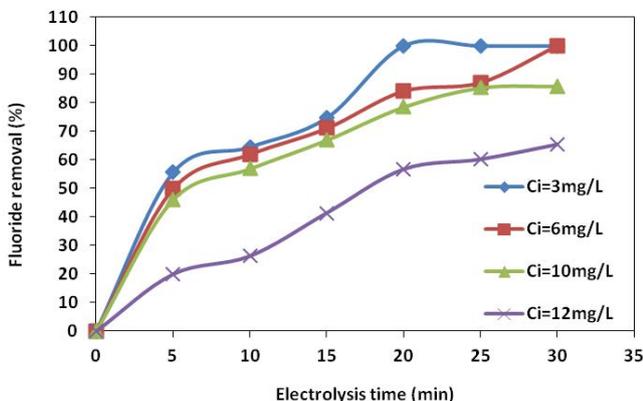


Fig. 8. Effect of the initial fluoride concentration on the fluoride removal as function of electrolysis time ($\text{pH}_i = 6$, $J = 0.27 \text{ mA/cm}^2$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $d_i = 1 \text{ cm}$).

Table 2

Time evolution necessary to reach the norm and the energy consumption according to the initial concentrations ($\text{pH}_i = 6$, $J = 0.27 \text{ mA/cm}^2$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $d_i = 1 \text{ cm}$)

C_i (mg/L)	t (min)	E (KWh/m ³)
3	10	0.0132
6	20	0.0264
10	25	0.0396
12	–	–

the effect of this parameter on the EC process. In order to determine an optimal distance between the electrodes used, we performed four EC tests with inter-electrode distances between 0.5 and 2 cm. The other factors remain invariant. The effect of the inter-electrode distance on the percentage of elimination is shown in Fig. 9.

The efficiency of EC process on defluorination is greater when the distance is shorter. The fluorine removal is maximum for 0.5 cm and it decreases to 55.78% for 2 cm. The obtained results corroborate Daneshvar et al. [42] hypothesis increasing the inter-electrode distance results in a decrease of the interactions between ions and the formed hydroxides [14,42]. Although the inter-electrode distance is a critical parameter of the EC, it acts strongly on energy consumption. It increases with the increase of the inter-electrode distance that increases the resistance (R) of the solution.

Knowing that:

$$R = \frac{\rho \times d_i}{S} \text{ (Ohm)} \quad (3)$$

where ρ : resistivity (Ohm/cm), d_i : inter-electrode distance (cm), S : active surface area of the electrodes (cm²).

From the experimental results in Table 3, as the inter-electrode distance increases, energy consumption increases and defluorination efficiency decreases. It can be concluded that the optimum distance to be used is equal to 0.5 cm. Indeed, it is a little difficult to work with very small distances on the industrial scale as well to avoid short circuits [36]. Higher values are not recommended to see the increase in

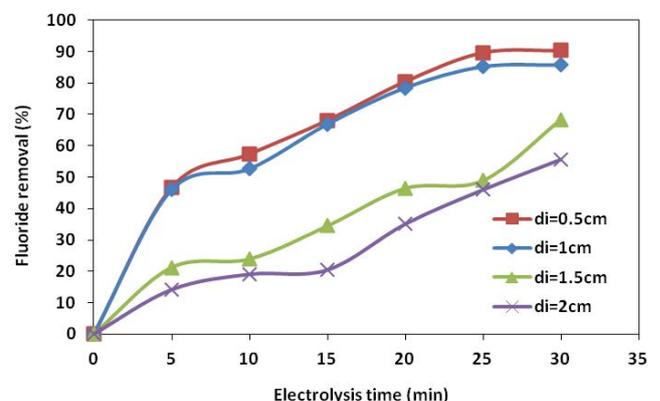


Fig. 9. Evolution of fluoride removal as a function of time for different inter-electrode distances ($\text{pH}_i = 6$, $J = 0.27 \text{ mA/cm}^2$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $C_i = 10 \text{ mg/L}$).

Table 3

Effect of current density on fluoride removal and energy consumption ($\text{pH}_i = 6$, $J = 0.27 \text{ mA/cm}^2$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $C_i = 10 \text{ mg/L}$)

d_i (cm)	Fluoride removal (%)	E (kWh/m ³)
0.5	88.65	0.0360
1.0	85.76	0.0396
1.5	68.4	0.0468
2.0	54.78	0.0468

ohmic resistance resulting in high consumption. The distance of 1 cm will be considered ideal for the sequel. It is recommended by several teams such as Kim et al. [43], Chen et al. [44] and Emamjomeh and Sivakumar [16].

3.7. Effect of surface/volume ratio

The surface/volume ratio (S/V) is defined by the active area of the electrodes divided by the volume processed. It has a remarkable influence on the kinetics of the coagulant formation reaction and the energy consumption. This parameter can therefore affect the elimination efficiency on the one hand and the cost of treatment on the other. We have tried to study the action of the variation of the ratio of the active surface of the electrodes on the EC process. Three tests were carried out for different S/V ratios: 3.6, 7.2 and 14.4 m⁻¹ and under the same current density (Fig. 10).

The experimental results show that when the ratio is increased the percentage of elimination increases. It is maximum for S/V = 14.4 m⁻¹ [12]. Increasing the S/V ratio increases energy consumption to 0.0936 kWh/m³. The active surfaces can manage the amount of dissolved aluminum that leads to the formation of coagulant and the distribution of flocs. We can also extract that the low surface area increases the EC duration. Accepted fluoride content in water (1.35 mg/L) are obtained with low surface/volume ratio (S/V = 7.2 m⁻¹) and low cost of treatment.

3.8. Effect of number of pairs of electrodes

To improve the performance of the fluoride removal process, we increased the number of sacrificial electrodes to increase the active surface area. The EC tests were taken under the same operating conditions with 1, 2 and 3 pairs of the electrodes (Fig. 11).

The results obtained shows that defluorination kinetics increase with increasing number of electrodes under the same imposed current. It is evident that the decrease in number of electrodes decreases the active surface area and consequently the amount of aluminum generated which disadvantages the formation of flocs [45].

Likewise, the increase in the S/V ratio is proportional to the number of electrodes, which is a very effective elimination. It is also possible to plot the variation of the elimination percentage and the current density as a function of the number of electrodes (Fig. 12). It is found that increasing the electrodes increases the elimination rate and thus a decrease in the current density.

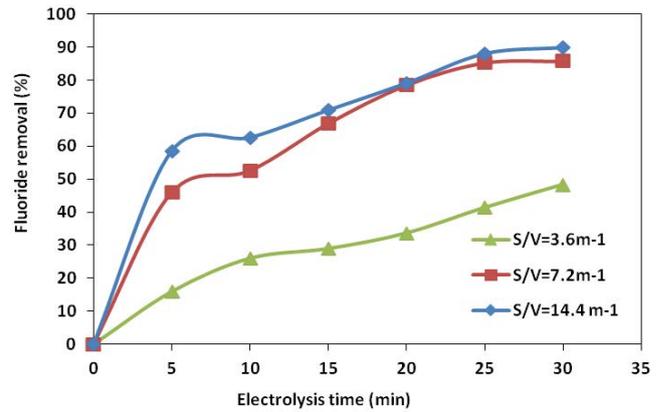


Fig. 10. Evolution of the fluorine removal with electrolysis time for different S/V ratio ($\text{pH}_i = 6$, $J = 0.27 \text{ mA/cm}^2$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $C_i = 10 \text{ mg/L}$, $d_i = 1 \text{ cm}$).

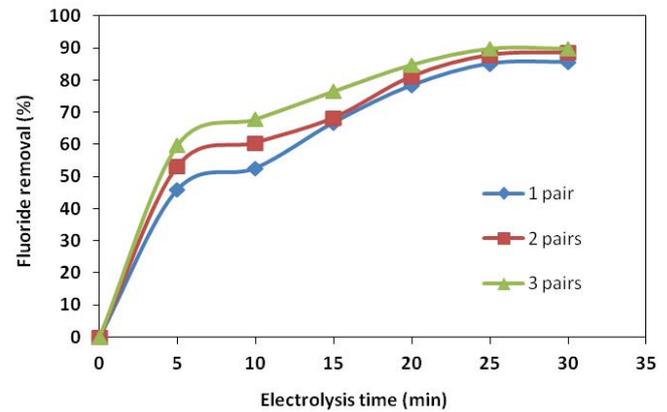


Fig. 11. Effect of the number of electrode pairs on the percentage of elimination as a function of time ($J = 0.27 \text{ mA/cm}^2$, $\text{pH}_i = 6$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $C_i = 10 \text{ mg/L}$, $d_i = 1 \text{ cm}$).

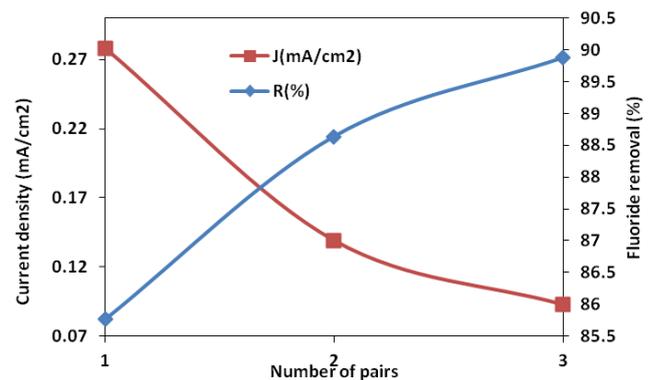


Fig. 12. Variation of the elimination percentage and the current density as a function of the number of electrodes ($J = 0.27 \text{ mA/cm}^2$, $\text{pH}_i = 6$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $C_i = 10 \text{ mg/L}$, $d_i = 1 \text{ cm}$).

The efficiency of defluorination by EC is higher than the active surface area is great to see a good generation of coagulants. The effect of the number of electrode pairs on energy consumption was also evaluated at 1, 2 and 3 pair(s) (Fig. 13

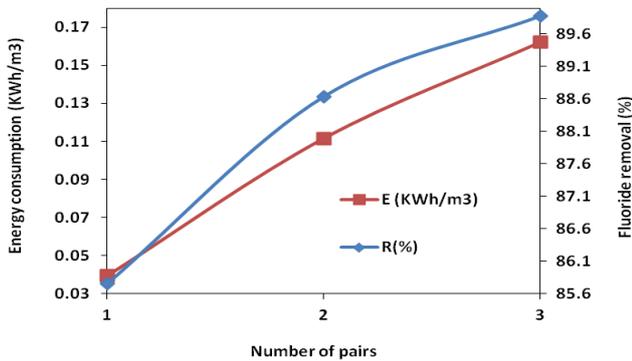


Fig. 13. Effect of the number of electrode pairs on fluoride removal ($J = 0.27 \text{ mA/cm}^2$, $\text{pH}_i = 6$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $C_i = 10 \text{ mg/L}$, $d_i = 1 \text{ cm}$).

Table 4

Effect of the number of electrode pairs on energy consumption ($J = 0.27 \text{ mA/cm}^2$, $\text{pH}_i = 6$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $C_i = 10 \text{ mg/L}$, $d_i = 1 \text{ cm}$)

Number of pairs	Fluoride removal (%)	CE (kW h/m ³)
1	85.76	0.0396
2	88.64	0.1116
3	89.88	0.162

and Table 4). According to the results obtained, the energy consumption is high up to 0.162 kWh/m^3 for 3 pairs of the electrodes.

3.9. Effect of Stirring speed

Agitation plays an important role in the EC process. It maintains the homogeneity of the medium and inhibits the formation of a concentration gradient in the electrolysis cell. The effect of stirring rate on the fluoride removal rate was varied from 0 to 600 rpm (Fig. 14).

As seen in (Fig. 14), fluoride removal was maximal at a stirring rate of 300 rpm with a percentage equivalent to 85.76% after 30 min. At this value, the formation of the flocs intimately associated with each other is higher and precipitation becomes easier [46,47].

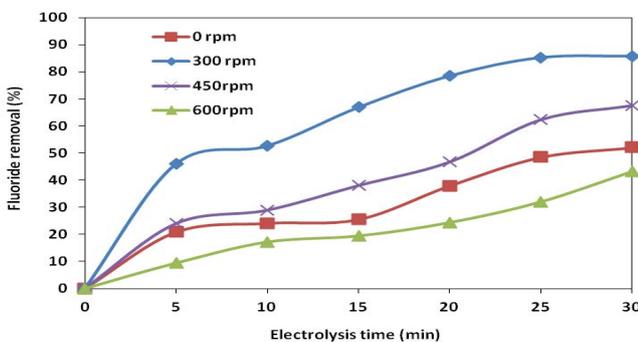


Fig. 14. Effect of stirring speed on fluoride removal as a function of time ($J = 0.27 \text{ mA/cm}^2$, $\text{pH}_i = 6$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $C_i = 10 \text{ mg/L}$, $d_i = 1 \text{ cm}$).

Without agitation, the percentage of elimination does not exceed 52.06%. However, beyond 300 rpm, a gradual reduction in the percentage of elimination is observed, respectively, from 67.64% to 43.06% at 450 and 600 rpm (Fig. 15). These results can be explained by the degradation of the flocs under the effect of strong agitation. Thus, at higher agitation, solubility of precipitate increases and formation of the inappropriate flocs over a period of time has occurred. It is important to note that the amount of settled sludge depends on the agitation rate. Without stirring, the solution appeared homogeneous and not clears [48,49].

3.10. Effect of connection mode

3.10.1. Bipolar connection mode

Only the two extreme electrodes are connected to one terminal of the generator. In this case, each intermediate electrode polarizes (in the direction of the current) and it is possible to identify 3 cells mounted in series and therefore all traversed by the same current $i = I$.

3.10.2. Monopolar connection mode

It consists of connecting the two extreme electrodes to the generator. For the others; each pair of neighboring electrodes will be interconnected. In this case where each electrode is active on one of its faces, it is possible to identify 2 cells in series traversed by the same current I .

In Table 5 and Fig. 16, the percentage of removal of the fluoride depends strongly on connection mode: 66.83% for the monopolar mode and 88.72 for the bipolar mode

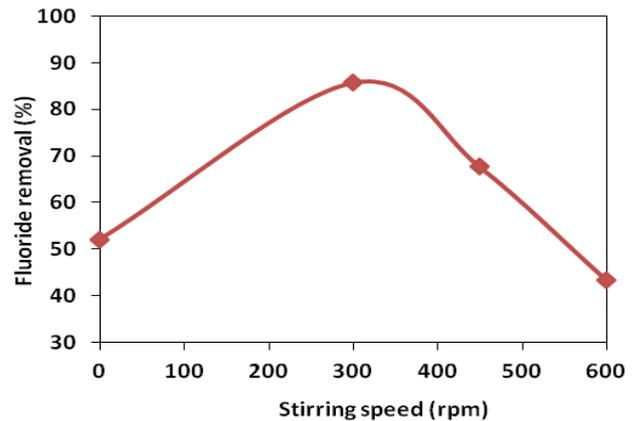


Fig. 15. Effect of stirring speed on fluoride removal ($J = 0.27 \text{ mA/cm}^2$, $\text{pH}_i = 6$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $C_i = 10 \text{ mg/L}$, $d_i = 1 \text{ cm}$).

Table 5

Effect of the mode of connection on fluoride removal and energy consumption ($J = 0.27 \text{ mA/cm}^2$, $\text{pH}_i = 6$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $C_i = 10 \text{ mg/L}$, $d_i = 1 \text{ cm}$)

Connection mode	Fluoride removal (%)	Energy (kWh/m ³)
Monopolar	66.83	0.0864
Bipolar	86.72	0.1116

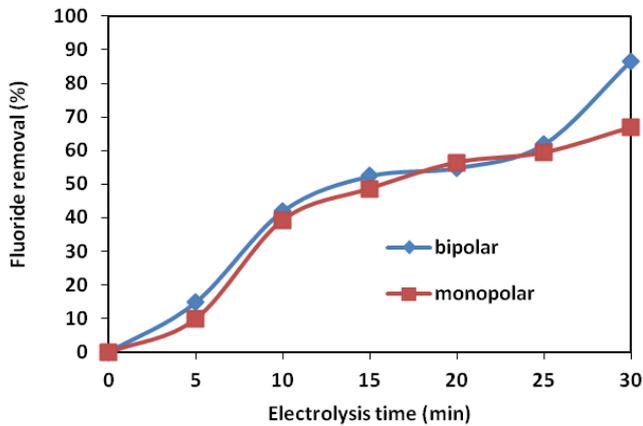


Fig. 16. Effect of connection mode on percent removal as a function of time ($J = 0.27 \text{ mA/cm}^2$, $\text{pH}_i = 6$, $[\text{NaCl}] = 0.5 \text{ g/L}$, $C_i = 10 \text{ mg/L}$, $d_i = 1 \text{ cm}$).

[50,51]. The latter increases the energy consumption to 0.1116 kWh/m^3 , like 0.0864 kWh/m^3 for monopolar connection of the electrodes. The different connection modes affect the value of the S/V ratio of depending on the active area of the electrodes in an EC cell. As we have already shown, when the S/V ratio is increased, the efficiency of the process increases with high energy consumption. However, it should be noted that the connection of the electrodes must be chosen so that we achieve maximum elimination with low energy consumption.

4. Kinetic and adsorption isotherm study of electrocoagulation on fluoride removal

4.1. Kinetic study

In the electrocoagulation process, the rate of fluoride removal was proportional to the initial fluoride concentration and the amount of corresponding hydroxide formed.

To evaluate the removal rate constant, further experiments were performed at the optimized conditions. The removal kinetics of fluoride on the amount of electrochemically dissolved aluminum oxyhydroxides were determined by pseudo-kinetic models. The rate of removal fluoride can be represented by the following pseudo-first-order equation [52]:

$$\frac{-dC}{dt} = k_1 C \tag{4}$$

where $C \text{ (mg/L)}$ represents the fluoride concentration, $k \text{ (min}^{-1}\text{)}$ is the rate constant, and $t \text{ (min)}$ is the electrolysis time.

The integration of the above Eq. (4) yields:

$$\log \frac{C_i}{C} = K_1 t \tag{5}$$

The pseudo-first rate constant K_1 can be calculated from the plot of $\log(C_i/C)$ versus electrolysis time (t).

Furthermore, for the pseudo-second-order reaction, above (Eq. 4) becomes [53]:

$$\frac{1}{C} - \frac{1}{C_i} = K_2 t \tag{6}$$

A plot graph between $(1/C - 1/C_i)$ vs. run time (t) gives the value of rate constant $K_2 \text{ (mg}^{-1} \text{ min}^{-1}\text{)}$.

In Table 6, the kinetics and isotherm data (rate constants and R^2 values) obtained from pseudo-first-order and pseudo-second-order kinetic models for the fluoride adsorption onto electro generated adsorbent. These results found that fluoride adsorption reaction follows pseudo-second-order model. The pseudo-second-order rate constant for the different fluoride concentrations studied was decreased in the range of 0.0629, 0.0261, 0.0149 and 0.0057 min^{-1} , respectively, for 3, 6, 10 and 12 mg/L . It can be confirmed that the rate constant decreases with increase in the initial concentration [54,55].

It could be due to the decrease in ratio of aluminum oxyhydroxides to the initial fluoride concentration, which eventually reduces the rate of fluoride removal, and subsequently the rate constant.

4.2. Adsorption isotherm

The study of isotherms was carried out to try to understand the phenomenon of adsorption of fluoride onto electro generated adsorbent. The experimental results for different initial fluoride concentration (from 3 to 12 mg/L) were taken for adsorption isotherm study.

The Langmuir model makes it possible to determine whether a monolayer is adsorbed and whether there has been no interaction between the adsorbed molecules. The Langmuir equation is valid for adsorbed monolayer with a well defined number of uniform and energy identical adsorption sites according to the following relation [56]:

$$q_e = \frac{q_m \times b \times C_e}{(1 + b \times C_e)} \tag{7}$$

where q_e : amount adsorbed at equilibrium (mg/g), q_m : adsorption capacity (mg/g), C_e : concentration of fluorine in solution at equilibrium (mg/L), b : adsorption energy constant.

Eq. (7) can be written as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{C_e \times q_m \times b} \tag{8}$$

Table 6
Kinetic rate constants with pseudo-first-order and pseudo-second-order models for fluoride adsorption

[F] (mg/L)	Pseudo-first-order model		Pseudo-second-order model	
	$K_1 \text{ (min}^{-1}\text{)}$	R^2	$K_2 \text{ (mg}^{-1} \text{ min}^{-1}\text{)}$	R^2
3	0.0871	0.922	0.0629	0.9799
6	0.0846	0.969	0.0261	0.9910
10	0.0719	0.9824	0.0144	0.9853
12	0.0391	0.9677	0.0053	0.9713

The Freundlich model is an empirical model which gives an indication of the heterogeneity of the adsorbent surface. The isotherm is applied to describe reversible adsorption and not limited to monolayer formation [57]. Mathematical expression of the Freundlich model is as follows:

$$q_e = K_f \times C_e^{1/n} \quad (9)$$

where q_e : amount adsorbed at equilibrium (mg/g), C_e : concentration of fluorine in solution at equilibrium (mg/L), K_f and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

A linear form of the Freundlich equation can be written in logarithmic form according to the following relation:

$$\log q_e = \log K_f + \frac{1}{n} \times C_e \quad (10)$$

The experimental results of fluoride adsorption were fitted to both Langmuir and Freundlich models as shown respectively in (Fig. 17). The calculated isotherm constants (q_m , b and K_f , $1/n$) and correlation coefficients are assembled in Table 7.

Based on the correlation coefficient (R^2), the adsorption isotherm with hydroxo aluminum complexes can be better described by the Langmuir isotherm model. The Langmuir isotherm equation represents a better fit with the experimental data than the Freundlich isotherm. The results fitted with the Langmuir and Freundlich equations showed that fluoride removal was achieved by a monolayer adsorption onto hydroxide aluminium, with a finite number of identical sites.

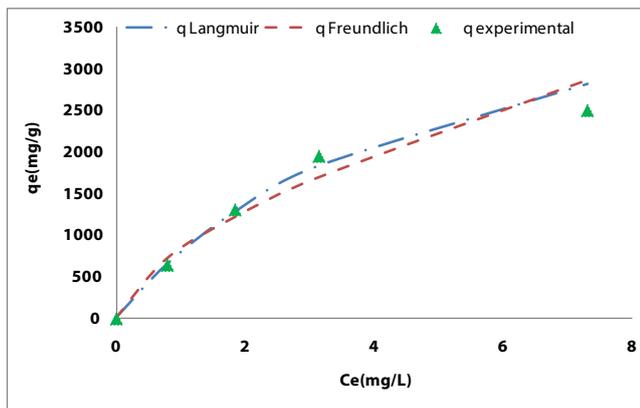


Fig. 17. Isotherm plot of equilibrium concentration vs. fluoride adsorbed per unit mass of adsorbent.

Table 7

Calculated isotherm parameters for Langmuir and Freundlich models

Langmuir isotherm		Freundlich isotherm	
R^2	0.9960	R^2	0.9508
q_m (mg/g)	4761	K_f ($\text{mg}^{-1} \text{min}^{-1}$)	0.0012
b	0.2	$1/n$	0.6240

5. Conclusion

In this study, the electrochemical removal of fluoride from aqueous media using aluminum as electrode materials has been investigated. It was found that optimum removal efficiencies were achieved at pH_i adjusted to 6, a current density of 0.27 mA/cm^2 , an NaCl dose of 0.5 g/L , S/V ratio of 7.2 m^{-1} and stirring speed equal to 300 rpm with two electrodes distant of 1 cm for an electrolysis time of 30 min . The obtained results showed that fluoride removal reached 85.76% for a low energy consumption of 0.0396 kWh/m^3 . The removal of fluoride increased with time, and the correlation coefficients for the kinetic plots obtained using different initial fluoride concentrations showed that the adsorption process followed a second-order kinetic model. The electrocoagulation has been modeled using adsorption isotherm models. Based on the correlation coefficient (R^2), the adsorption isotherm can be better described by the Langmuir isotherm model. In view of the fact that fluoride was completely removed for initial concentration of 3 and 6 mg/L , EC could be regarded as a potential technique for the treatment of ground water containing fluoride.

References

- [1] A. Ben Nasr, Performances of Physico-Chemical and Membranes Processes for the Elimination of Fluoride Ions In drilling Waters: Application to Tunisian Waters, Ph.D. Thesis, University of Sfax, Tunisia, 2013.
- [2] L.P. Mccaffrey, Distribution and Causes of High Fluoride Groundwater in the Western Bushveld Area of South Africa, Ph.D. Thesis, University of Cape Town, South Africa, 1998.
- [3] S. Vasudevan, J. Lakshmi, G. Sozhan, Studies on a Mg–Al–Zn alloy as an anode for the removal of fluoride from drinking water in an electrocoagulation process, Clean-Soil Air Water, 37 (2009) 372–378.
- [4] F. Shen, X. Chen, P. Gao, G. Chen, Electrochemical removal of fluoride ions from industrial wastewater, Chem. Eng. Sci., 58 (2003) 987–993.
- [5] Meenakshi, R.C. Maheshwari, Fluoride in drinking water and its removal, J. Hazard. Mater., 137 (2006) 456–463.
- [6] WHO (World Health Organization), Guidelines for Drinking Water Quality: Health Criteria and Supporting Information, Vol. 2, World Health Organization, Geneva, Switzerland, 1984.
- [7] A. Ben Nasr, C. Charcosset, R. Ben Amar, K. Walha, Defluoridation of water by nanofiltration, J. Fluorine Chem., 150 (2013) 92–97.
- [8] A. Ben Nasr, K. Walha, F. Puel, D. Mangin, R. Ben Amar, C. Charcosset, Precipitation and adsorption during fluoride removal from water by calcite in the presence of acetic acid, Desal. Wat. Treat., 52 (2014) 2231–2240.
- [9] D. Ghosh, C.R. Medhi, M.K. Purkait, Treatment of fluoride containing drinking water by electrocoagulation using monopolar and bipolar electrode connections, Chemosphere, 73 (2008) 1393–1400.
- [10] K. Brahmi, W. Bouguerra, H. Belhsan, E. Elaloui, M. Loungou, Z. Tlili, B. Hamrouni, Use of Electrocoagulation with aluminum electrodes to reduce hardness in Tunisian phosphate mining process water, Mine Water Environ., 35 (2016) 310–317.
- [11] K. Brahmi, B. Hamrouni, Removal of zinc ions from synthetic and industrial Tunisian wastewater by electrocoagulation using aluminum electrodes, Desal. Wat. Treat., 56 (2015) 2689–2698.
- [12] A. Barhoumi, S. Ncib, W. Bouguerra, B. Hamrouni, E. Elaloui, Combining adsorption on activated carbon with electrocoagulation process for copper removal from used water, Desal. Wat. Treat., 83 (2017) 212–221.
- [13] D.J. Cebula, R.H. Ottewill, J. Ralston, P.N. Pusey, Investigations of microemulsions by light scattering and neutron scattering, J. Chem. Soc., Faraday Trans. 1 F, 77 (1981) 1457–1735.

- [14] G. Mouedhen, M. Feki, M. De Petris Wery, H.F. Ayedi, Behavior of aluminum electrodes in electrocoagulation process, *J. Hazard. Mater.*, 150 (2008) 124–135.
- [15] C.Y. Hu, S.L. Lo, W.H. Kuan, Effects of the molar ratio of hydroxide and fluoride to Al(III) on fluoride removal by coagulation and electrocoagulation, *J. Colloid Interface Sci.*, 283 (2005) 472–476.
- [16] M.M. Emamjomeh, M. Sivakumar, An empirical model for defluorination by batch monopolar electrocoagulation/flotation (ECF) process, *J. Hazard. Mater.*, 131 (2006) 118–125.
- [17] D. Ghosh, C.R. Medhi, M.K. Purkait, Techno-economic analysis for the electrocoagulation of fluoride-contaminated drinking water, *Toxicol. Environ. Chem.*, 93 (2011) 424–437.
- [18] M.M. Naim, A.A. Moneer, G.F. El-Said, Defluorination of commercial and analar sodium fluoride solutions without using additives by batch electrocoagulation-flotation technique, *Desal. Wat. Treat.*, 44 (2012) 110–117.
- [19] M.A. Sandoval, R. Fuentes, J.L. Nava, I. Rodríguez, Fluoride removal from drinking water by electrocoagulation in a continuous filter press reactor coupled to a flocculator and clarifier, *Sep. Purif. Technol.*, 134 (2014) 163–170.
- [20] K. Govindan, M. Raja, S.U. Maheshwari, M. Noel, Y. Oren, Comparison and understanding of fluoride removal mechanism in Ca^{2+} , Mg^{2+} and Al^{3+} ion assisted electrocoagulation process using Fe and Al electrodes, *J. Environ. Chem. Eng.*, 3 (2015) 1784–1793.
- [21] E.N. Kapinus, I.A. Revelskaya, V.O. Ulogovb, Yu.A. Lyalikov, Simultaneous determination of fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate in aqueous solutions at 10^{-9} to $10^{-8}\%$ level by ion chromatography, *J. Chromatogr. B*, 800 (2004) 321–323.
- [22] C.B. Shivayogimath, S. Punage, Optimization of parameters for fluoride removal by electrocoagulation using aluminum electrodes in monopolar parallel combination, *J. Eng. Res. Technol.*, 3 (2014) 1276–1280.
- [23] V. Khatibikamal, A. Torabian, F. Janpoor, G. Hoshyaripour, Fluoride removal from industrial wastewater using electrocoagulation and its adsorption kinetics, *J. Hazard. Mater.*, 179 (2010) 276–280.
- [24] N. Drouiche, S. Aoudj, M. Hecini, N. Ghaffour, H. Lounici, N. Mameri, Study on the treatment of photovoltaic wastewater using electrocoagulation: fluoride removal with aluminium electrodes-characteristics of products, *J. Hazard. Mater.*, 169 (2009) 65–69.
- [25] U.T. Un, A.S. Kopalal, U.B. Ogutveren, Fluoride removal from water and wastewater with a batch cylindrical electrode using electrocoagulation, *Chem. Eng. J.*, 223 (2013) 110–115.
- [26] H. Zhao, H. Liu, J. Qu, Effect of pH on the aluminum salts hydrolysis during coagulation process: formation and decomposition of polymeric aluminum species, *J. Colloid Interface Sci.*, 330 (2009) 105–112.
- [27] R.M. Smith, A.E. Martell, *Cristal Stability Constants*, Vol. 4, Inorganic Complexes, Plenum Press, New York, London, 1976.
- [28] J. Zhu, H. Zhao, J. Ni, Fluoride distribution in electrocoagulation defluorination process, *Sep. Purif. Technol.*, 56 (2007) 184–191.
- [29] U.T. Un, A.S. Kopalal, U.B. Ogutveren, Electrocoagulation of vegetable oil refinery wastewater using aluminum electrodes, *J. Environ. Manage.*, 90 (2009) 428–433.
- [30] C.-Y. Hu, S.-L. Lo, W.-H. Kuan, Simulation the kinetics of fluoride removal by electrocoagulation (EC) process using aluminum electrodes, *J. Hazard. Mater.*, 145 (2007) 180–185.
- [31] M.M. Emamjomeh, M. Sivakumar, A.S. Varyani, Analysis and the understanding of fluoride removal mechanisms by an electrocoagulation/flotation (ECF) process, *Desalination*, 275 (2011) 102–106.
- [32] P.K. Holt, G.W. Barton, C.A. Mitchell, The future for electrocoagulation as a localised water treatment technology, *Chemosphere*, 59 (2005) 355–367.
- [33] B. Palahouane, N. Drouiche, S. Aoudj, K. Bensadok, Cost-effective electrocoagulation process for the remediation of fluoride from pretreated photovoltaic wastewater, *J. Ind. Eng. Chem.*, 22 (2015) 127–131.
- [34] A.H. Essadki, M. Bennajah, B. Gourich, C. Vial, M. Azzi, H. Delmas, Electrocoagulation/electroflotation in an external-loop airlift reactor-application to the decolorization of textile dye wastewater: a case study, *Chem. Eng. Process.*, 47 (2008) 1211–1223.
- [35] M. Bayramoglu, M. Eyvaz, M. Kobya, Treatment of the textile wastewater by electrocoagulation: economical evaluation, *Chem. Eng. J.*, 128 (2007) 155–161.
- [36] N. Mameri, A.R. Yeddou, H. Lounici, D. Belhocine, H. Grib, B. Bariou, Defluorination of Septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrodes, *Water Res.*, 32 (1998) 1604–1612.
- [37] K. Bensadok, S. Benammar, F. Lapique, G. Nezzal, Electrocoagulation of cutting oil emulsions using aluminium plate electrodes, *J. Hazard. Mater.*, 152 (2008) 423–430.
- [38] M. Khemis, J.-P. Leclerc, G. Tanguy, G. Valentin, F. Lapique, Treatment of industrial liquid wastes by electrocoagulation: experimental investigations and an overall interpretation model, *Chem. Eng. Sci.*, 61 (2006) 3602–3609.
- [39] B. Merzouk, B. Gourich, A. Sekki, K. Madani, M. Chibane, Removal turbidity and separation of heavy metals using electrocoagulation-electroflotation technique: a case study, *J. Hazard. Mater.*, 164 (2009) 215–222.
- [40] Q. Zuo, W. Chen, X. Li, G. Chen, Combined electrocoagulation and electroflotation for removal of fluoride from drinking water, *J. Hazard. Mater.*, 159 (2008) 452–457.
- [41] K. Missaoui, W. Bouguerra, G.B. Salha, B. Hamrouni, Defluorination of South Tunisian Brackish Water by electrocoagulation using experimental design methodology, *Int. J. Eng. Res. Technol.*, 3 (2014) 2908–2916.
- [42] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters, *J. Hazard. Mater.*, 129 (2006) 116–122.
- [43] T.H. Kim, C. Park, E.B. Shin, S. Kim, Decolorization of disperse and reactive dyes by continuous electrocoagulation process, *Desalination*, 150 (2002) 165–175.
- [44] C.L. Lai, S.H. Lin, Electrocoagulation of chemical mechanical polishing (CMP) wastewater from semiconductor fabrication, *Chem. Eng. J.*, 95 (2003) 205–211.
- [45] International Conference on Chemical, Environmental and Biological Sciences (CEBS-2015), Dubai (UAE), March 18–19, 2015.
- [46] O.T. Can, M. Bayramoglu, M. Kobya, Decolorization of reactive dye solutions by electrocoagulation using aluminum electrodes, *Ind. Eng. Chem. Res.*, 42 (2003) 3391–3396.
- [47] A. Gürses, M. Yalçın, Ç. Doğar, Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables, *Waste Manage.*, 22 (2002) 491–499.
- [48] A.S. Kopalal, O.B. Ögütveren, Removal of nitrate from aqueous solutions by electrodialysis, *Int. J. Environ. Stud.*, 59 (2002) 323–329.
- [49] *Engineering Research (IJMER) www.iimer.com*, 3 (2013, Jan-Feb) 101–108, ISSN: 2249-6645.
- [50] N. Modirshahla, M.A. Behnajady, S. Kooshaiian, Investigation of the effect of different electrode connections on the removal efficiency of Tartrazine from aqueous solutions by electrocoagulation, *Dyes Pigm.*, 74 (2007) 249–257.
- [51] N. Modirshahla, M.A. Behnajady, S. Mohammadi-Aghdam, Investigation of the effect of different electrodes and their connections on the removal efficiency of 4-nitrophenol from aqueous solution by electrocoagulation, *J. Hazard. Mater.*, 154 (2008) 778–786.
- [52] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, *Kungliga Svenska, Vetenskapsakademiens, Handlingar*, 24 (1998) 1–39.
- [53] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, *Process Biochem.*, 34 (1999) 451–465.
- [54] M.G. Sujana, G. Soma, N. Vasumathi, S. Anand, Studies on fluoride adsorption capacities of amorphous Fe/Al mixed hydroxides from aqueous solutions, *J. Fluorine Chem.*, 130 (2009) 749–754.
- [55] N. Balasubramanian, T. Kojima, C.A. Basha, C. Srinivasakannan, Removal of arsenic from aqueous solution using electrocoagulation, *J. Hazard. Mater.*, 167 (2009) 966–969.
- [56] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica, and platinum, *J. Am. Chem. Soc.*, 40 (1918) 1361–1368.
- [57] H.M.F. Freundlich, *Über Die Adsorption in Lösungen*, *Zeitschrift für Physikalische Chemie*, Leipzig, 57A (1906) 385–470.