

Defluoridation of South Tunisian Brackish Water by Electrocoagulation using Experimental Design Methodology

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Abstract— Fluoride ion in water has both beneficial and harmful effects on the environment and the human. Waters with high fluoride content are usually found at the foot of high mountains and in areas with geological deposits of marine origin. Face to the rarefaction of the resources in drinkable water of good quality, the treatment of natural south Tunisian water with an excessive content of fluoride will become a necessity. Various treatment technologies, based on the principle of precipitation, ion exchange, membrane and adsorption process have been proposed and are tested for fluoride removal efficiency from drinking water as well as industrial effluents. Fluoride removal from aqueous solution was investigated using electrocoagulation process in reason of the efficiency and the simplicity of the process.

Preliminary experiments were carried out to study the effect of some operating parameters such as: initial pH, initial fluoride concentration, the conductivity of the solution, the inter-electrode distance, the number of pair of electrodes, the connection mode and current density (J). Experimental design methodology using two-level full factorial design was applied to evaluate statistically the most significant operating parameters. Therefore, three operating parameters which are supposed to affect the removal efficiency were chosen: initial fluoride concentration, current density and initial pH. From the statistical analysis, it is inferred that current density (J) and initial fluoride concentration had a considerable effect on fluoride removal by EC. Initial fluoride concentration has a positive effect unlike current density has a negative effect. Nevertheless, initial pH was estimated as unimportant factor. Experiment tests were performed to evaluate the efficiency of electrocoagulation process

for south Tunisian brackish water with high fluoride concentration. The obtained results showed that fluoride removal reached 55%.

Keywords— *defluoridation, electrocoagulation, full factorial design, brackish Tunisian water.*

I. INTRODUCTION

The fluoride occurs mainly as sellaite MgF_2 , fluorspar CaF_2 , cryolite (Na_3AlF_6), and fluorapatite ($3Ca_3(PO_4)_2 \cdot Ca(F,Cl)_2$) [1]. Fluorspar is found in sedimentary rocks while cryolite is found in igneous rocks. These fluoride minerals are nearly insoluble in water. Hence fluorides will be present in groundwater only when conditions favor their dissolution or high fluoride containing effluents are discharged to the water bodies from industries. Fluoride removal receives much attention due to the dental and skeletal fluorosis caused by the excessive intake of fluoride [2]. In the south Tunisian brackish water, the range level of fluoride ions is situated between 1.5 and 2.5 $mg L^{-1}$. However, in the region of Gafsa fluoride content greater than 2.5 $mg L^{-1}$ are encountered [3]. The World Health Organization (WHO) fixed the maximum fluoride concentration in drinking water as 1.5 $mg L^{-1}$. In excess of 1.5-2.0 $mg L^{-1}$ fluoride is known to cause permanent gray or black mottling of teeth enamel and the long-term intake of 3-10 $mg L^{-1}$ may result in abnormal bone growth in both humans and animals. Invertebrates and fish in fresh water are also very sensitive to fluoride toxicity [4]. Many methods have been developed to remove excessive fluoride from drinking water.

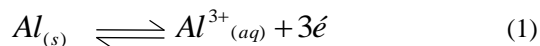
Different techniques like adsorption, membrane separation, ion-exchange, hybrid techniques and electrocoagulation (EC) were reported for the removal of fluoride from drinking water [5].

Electrochemical technology contributes in many ways to a cleaner environment and covers a very broad range of technology [6, 7]. Electrocoagulation (EC) is an efficient method used for treating various process effluents. In an

electrocoagulation (EC) process, no addition of chemicals is necessarily needed. Small volume of sludge is produced, comparing with that in classical chemical process, which can be easily removed by decantation. EC involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from, respectively, aluminum or iron electrodes. The metal ion generation takes place at the anode; hydrogen gas is released from the cathode. EC is a complex process occurring via serial steps such as electrolytic reactions at electrode surfaces, formation of coagulants in aqueous phase, adsorption of soluble or colloidal pollutants on coagulants which are removed by sedimentation or flotation [8].

Aluminium was reported to be very effective and successful in pollutant removal at favorable operating conditions. The electrode and bulk reactions for the removal of fluoride are summarized as follows:

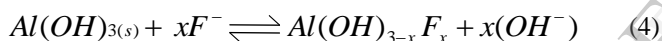
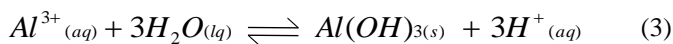
- At the anode:



- At the cathode:



Bulk:



The major interaction mechanism considered in recent years is adsorption followed by precipitation. Al^{3+} and OH^- ions generated by electrode reactions (1) and (2) react to form various monomeric species such as $Al(OH)^{2+}$; $Al(OH)_2^+$; $Al_2(OH)_2^{2+}$; $Al(OH)_4^-$ and polymeric species such as $Al_6(OH)_{15}^{3+}$; $Al_7(OH)_{17}^{4+}$; $Al_8(OH)_{20}^{4+}$; $Al_{13}O_4(OH)_{24}^{7+}$; $Al_{13}(OH)_{34}^{5+}$, which are transformed mostly into $Al(OH)_{3(s)}$ according to complex precipitation kinetics (3). Furthermore, this $Al(OH)_3$ complex is believed to have strong fluoride adsorption capacity [5].

The aim of this work is to remove fluoride from water by electrocoagulation. Several parameters : initial pH (pH_i), initial fluoride concentration ($[F^-]_0$), the conductivity of the solution (σ_i), the inter-electrode distance (d_{ie}), the number of pair of electrodes, the connection mode and current density (J) were studied. In the subsequent step the experimental design methodology using two-level full factorial design was applied to investigate the influence of the principal experimental parameters. Then the efficiency of electrocoagulation process was evaluated for south Tunisian brackish water containing high fluoride concentration.

II. MATERIAL AND METHODS

A. Analytical Methods

The fluoride concentrations were measured by means of a fluoride-selective electrode (Radiometer analytical- HACH). Total fluoride concentration was measured after mixing with total ionic strength adjustment buffer (TISAB) according to the Methods of Examination of Water and Wastewater1.

B. Electrocoagulation Test

A laboratory-scale reactor used to conduct EC experiments was a beaker with a working volume of about 2 L. Electrode assembly is the heart of the present treatment facility. Two groups of alternating electrodes being cathode and anode, made from plates of aluminum with dimensions of (8 - 7 - 0.2 cm) were arranged vertically. The electrodes assembly was connected to DC power supply (elc AL 924A) providing current and voltage in the range of (0 - 10 A) and (0 - 30 V). A gentle magnetic stirring rate of about 200 rpm was applied to the electrolyte in all tests. Electrolyte volume used was 2 L. All experiments were performed at around 25°C and were triplicated. Electrocoagulation unit is schematically shown in Fig. 1.

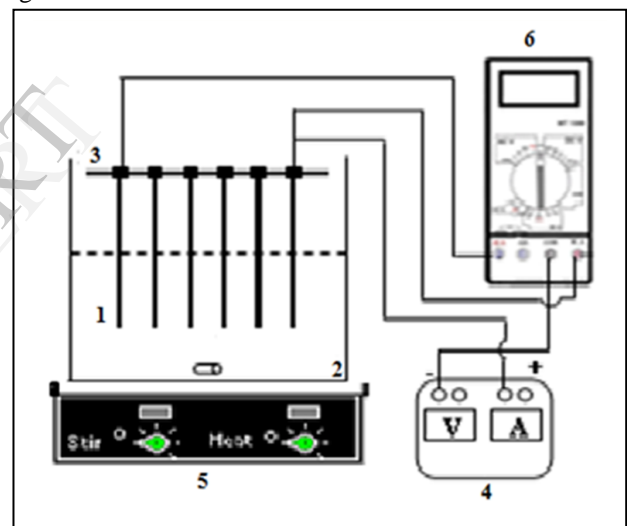


Fig. 1. Schematic diagram of electrocoagulation unit, ((1) aluminium electrodes; (2) treated solution; (3) electrodes support; (4) DC power supply; (5) magnetic stirrer; (6) multimeter).

Before the EC test and in order to avoid any interference and ensure surface reproducibility, electrodes were prepared as follows:

- ✓ Mechanically polished underwater with abrasive paper,
- ✓ Cleaned in NaOH solution (2 mol/L) for 2 min,
- ✓ Rinsed with distilled water,
- ✓ Cleaned in HCl solution (2 mol/L) for 2 min,
- ✓ Rinsed with distilled water,
- ✓ Dried with absorptive paper.

The initial pH of the solutions was adjusted by adding either HCl (0.1 mol/L) or NaOH (0.1 mol/L). NaCl was used

as supporting electrolyte to adjust the initial conductivity of the solution. For each experiment, the residual fluoride concentrations in the samples filtered through 0.45 micron filter paper (Millipore) were determined. The percentage of fluoride removed (%F) is given as:

$$\% F^{-} = 100 \cdot \left(1 - \frac{C_f}{C_0}\right) \quad (5)$$

Where C_0 and C_f are the initial and residual fluoride concentration in the solution.

III. RESULTS AND DISCUSSION

A. The effect of the initial pH

It has been established that the pH has a considerable influence on the performance of EC process. Indeed, the nature and the efficiency of the involved electrochemical and chemical reactions are intimately related to the pH level in the system. To investigate this effect, a series of experiments were carried out with an initial pH varying in the range pH 4 - 9. Different initial concentrations (3; 6; 9 and 12 mg L⁻¹) of fluoride were considered for the experiments.

Fig. 2. depicts the evolution of fluoride removal as function of the initial pH.

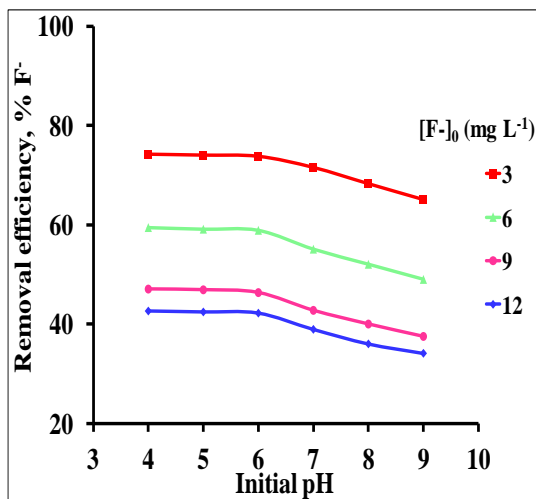


Fig. 2. Effect of the initial pH on fluoride removal %F⁻ ($\sigma_i = 9$ mS cm⁻¹, $J = 0.89$ mA cm⁻², $d_{ie} = 1$ cm and $t_{EC} = 20$ min).

From Figure 2, similar behaviour has been observed for all studied fluoride concentrations. It was observed that the variation of fluoride removal was negligible, in the region of pH_i of 4 - 6. For pH_i values higher than 6, the percentage of fluoride removal decreased significantly. At pH = 6, the formation of Al(OH)_{3(s)} and fluoroaluminium complexes were promoted.

Emamjomeh et al. [9] conducted a study to better understand the defluoridation mechanism of electrocoagulation by aluminium electrodes, and accounted for the fluoride complexes AlF^{2+} , AlF_2^+ , AlF_3 and AlF_4^- . They found that solid cryolite appeared in the pH range of 5 - 6, and by increasing the pH to 6 - 8 aluminium hydroxofluoride formation was maximized, which was the main mechanism for

defluoridation. They also found that fluoroaluminium complexes predominated in the acid solution until Al(OH)₃ precipitated. The fluoride removal efficiency decreased as the pH was increased from 8 to 10 [10]. According to obtained experimental results, all EC experiments were conducted at optimal pH_i = 6.

B. The effect of the initial conductivity

The chloride ion is often used in the electrocoagulation process to increase conductivity; however, it also has corrosive properties, and even at low concentrations results in breakdown of the passivating film through pitting corrosion [10]. The conductivity of the solution was adjusted to the desired levels upon addition of supporting electrolyte NaCl.

The effect of initial conductivity on the fluoride removal was examined. From Fig. 3, experimental results showed that fluoride removal increased slowly with increasing initial conductivity. The effect of initial conductivity on the energy consumption was evaluated (Fig. 4).

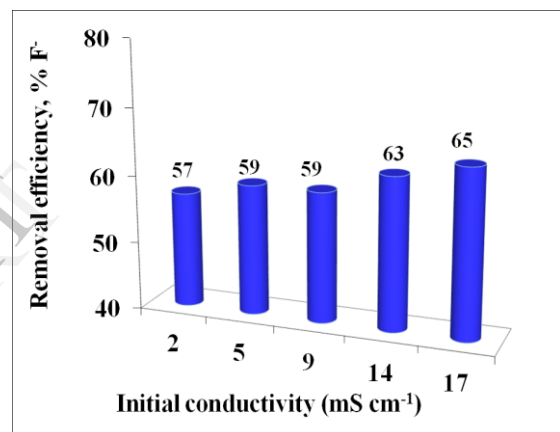


Fig. 3. Effect of the initial conductivity on fluoride removal %F⁻, ($[F^{-}]_0 = 6$ mg L⁻¹, pH = 6, $J = 0.45$ mA cm⁻², $d_{ie} = 1$ cm and $t_{EC} = 20$ min).

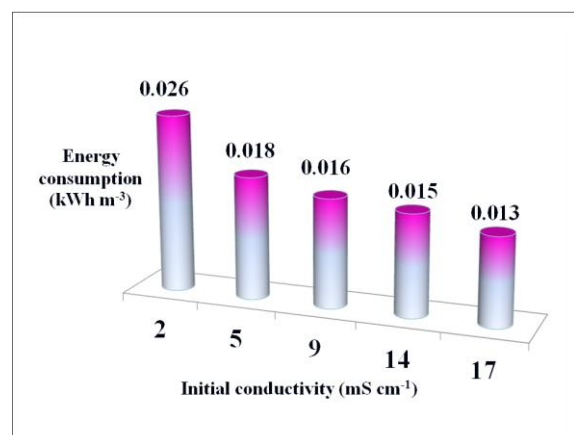


Fig. 4. Effect of the initial conductivity on energy consumption, ($[F^{-}]_0 = 6$ mg L⁻¹, pH = 6, $J = 0.45$ mA cm⁻², $d_{ie} = 1$ cm and $t_{EC} = 20$ min).

The addition of NaCl would also lead to the decrease in power consumption because of the increase in conductivity [10]. Obtained results confirmed that high conductivity values result in low energy consumption under the same current density. Increasing initial conductivity leads to energy consumption decrease due to relationship between conductivity and resistance: the conductivity stated as the inverse of the resistivity and the resistance is proportional to the resistivity.

However, if the addition of NaCl is beneficial in terms of power consumption, it can also induce overconsumption of aluminum electrodes corrosion if the concentration is high. Also, dissolution becomes irregular and sensitive to the mechanism of the EC [11]. Accordingly, all EC experiments were conducted at optimal initial conductivity around 5 mS cm^{-1} , to improve fluoride removal efficiency and minimize energy consumption.

C. The effect of the initial fluoride concentration

In the fluoride removal process by electrocoagulation, initial fluoride concentration is an important parameter. To determine the effect of the initial concentration of fluoride, different tests were carried out with different initial fluoride concentration from 3 up to 12 mg L^{-1} . Removal efficiency of fluoride and energy consumption were evaluated for different initial fluoride concentration studied (Figures 5 and 6).

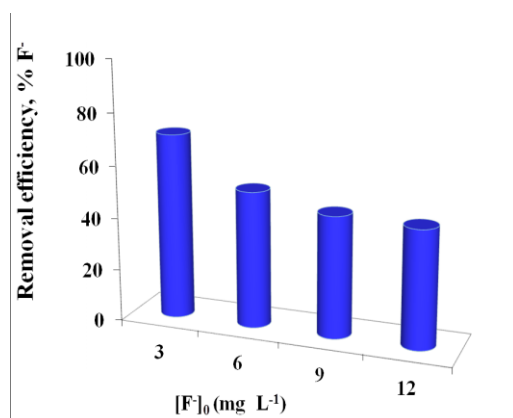


Fig. 5. Effect of the initial fluoride concentration on fluoride removal %F⁻, (pH = 6, $J = 0.45 \text{ mA cm}^{-2}$, $\sigma_i = 9 \text{ mS cm}^{-1}$, $d_{ie} = 1 \text{ cm}$ and $t_{EC} = 20 \text{ min}$).

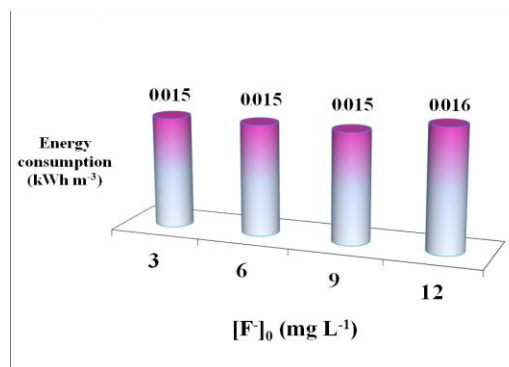


Fig. 6. Effect of the initial fluoride concentration on fluoride removal %F⁻, (pH = 6, $J = 0.45 \text{ mA cm}^{-2}$, $\sigma_i = 9 \text{ mS cm}^{-1}$, $d_{ie} = 1 \text{ cm}$ and $t_{EC} = 20 \text{ min}$).

Considering (Figure 5), it was observed that the removal efficiency of fluoride was closely related with its initial concentration. Fluoride removal decreases from 71% to 45% for initial fluoride concentration 3 and 12 mg L^{-1} respectively.

As the current density was kept constant so the production of the aluminium cation remained fixed and therefore with an increase in initial fluoride concentration, the complex formation process between the amorphous aluminium hydroxide and fluoride was insufficient [5]. Experimental results revealed that EC process is effective in waters with low or medium levels of fluoride. As shown in (Figure 6), the effect of the initial fluoride concentration on energy consumption is negligible.

D. The effect of Inter-Electrode Distance

Several tests were first performed to understand how EC efficiency varies with inter-electrode distance. Fluoride removal efficiency and energy consumption was examined for inter-electrode distance ranged from 1.0 to 7.0 cm. The effect of inter-electrode distance on the fluoride removal efficiency is shown in Figure 7.

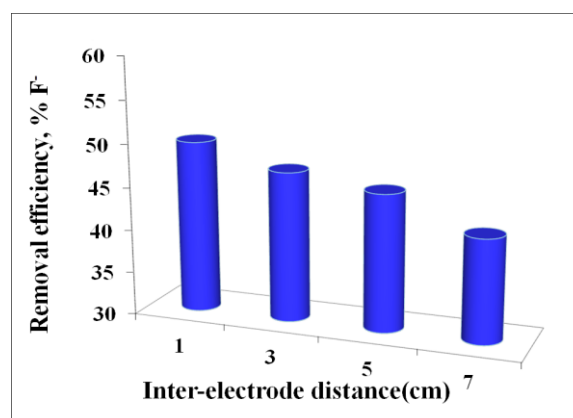


Fig. 7. Effect of inter-electrode distance on fluoride removal %F⁻, ($[F]_0 = 6 \text{ mg L}^{-1}$, pH = 6, $\sigma_i = 9 \text{ mS cm}^{-1}$, $J = 0.45 \text{ mA cm}^{-2}$ and $t_{EC} = 20 \text{ min}$).

When the inter-electrode distance decreases, the fluoride removal efficiency increases slightly. The increasing of fluoride removal in the less distance is probably resulting from the increase of electrostatic interactions [12].

Furthermore, in an electrochemical process, the most important economical parameter is energy consumption W (kWh m^{-3}). This parameter is calculated from the following expression:

$$W = \frac{U \cdot I \cdot t_{EC}}{V} \quad (6)$$

where U is the applied tension (V), I is the current intensity (A), t_{EC} is the time of EC (s) and V is the volume (m^3) of fluoride solution.

Applied tension could be explained with the following equation:

$$U = I \cdot R \quad (7)$$

where R is the resistance (Ohm).

From Eqs. (6) and Eqs. (7), the following equation could be obtained:

$$W = \frac{I^2 \cdot R \cdot t_{EC}}{V} \quad (8)$$

Inter-electrode distance has an effect on the amount of electrical energy introduced into the system to generate an electric field and induce motion of ions [12]. Figure 3 depicts the evolution of the energy consumption vs. inter-electrode distance. Globally, energy consumption increases with inter-electrode distance. This could be explained by the increase of the solution resistance, according to the following expression:

$$R = \frac{\rho \cdot d_{ie}}{S_a} \quad (9)$$

Where ρ is the resistivity (Ohm cm), d_{ie} is the inter-electrode distance (cm) and S_a is the total active surface (cm^2).

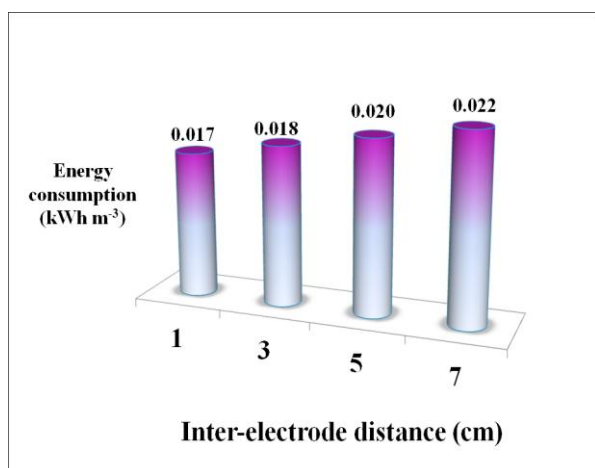


Fig. 8. Effect of inter-electrode distance on energy consumption, ($[F^-]_0 = 6 \text{ mg L}^{-1}$, $\text{pH} = 6$, $\sigma_i = 9 \text{ mS cm}^{-1}$, $J = 0.45 \text{ mA cm}^{-2}$ and $t_{EC} = 20 \text{ min}$).

Obtained results showed that the highest fluoride removal with the lowest energy consumption was reached for $d_{ie} = 1 \text{ cm}$. Therefore, all EC experiments were conducted at optimal $d_{ie} = 1 \text{ cm}$.

E. The effect of number of pair of electrodes and Connection Mode

The number of pair of electrodes (or the ratio (S/V) defined by the total active surface of electrodes divided by the volume of treated solution) and electrode connection mode are among the factors that may greatly influence the effectiveness of EC process. In order to improve the fluoride removal, the number of pair of electrodes was investigated under the same current density at 1; 2 and 3 pair(s) for (S/V) ratio respectively at (11.2 ; 22.4 and 33.6 m^{-1}). Two different electrode connections (mono-polar (M.P) and bi-polar (B.P)) were examined for choosing the better alternative. Schematic diagram of (M.P) and (B.P) electrochemical cell is shown in Figure 9.

It is basic to mention that in the B.P connection (Figures

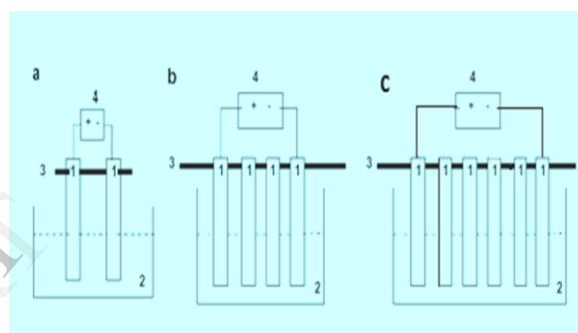


Fig. 9. Schematic diagram of electrochemical cell. (a) M.P connection (1 pair);(b) B.P connection (2 pairs) and (c) B.P connection (3 pairs), (1) aluminium electrodes;(2) treated solution; (3) electrode support; and (4) DC power supply.

9(b)-(c)) multiple electrodes were used while only the extreme electrodes are connected to the power supply. Every electrode excluding the electrodes at the end acts as an anode on one side and cathode on the other side. Each adjacent electrode pair acts as single unit. In such condition, induced polarization took place when voltage was applied to the end electrodes so that the inner electrodes started acting as a secondary cells. Therefore, the total assembly was bipolarized with a primary and a secondary cells acting together. Effect of the number of pair of electrodes and electrode connection mode for the fluoride removal by EC is shown in Figure 10.

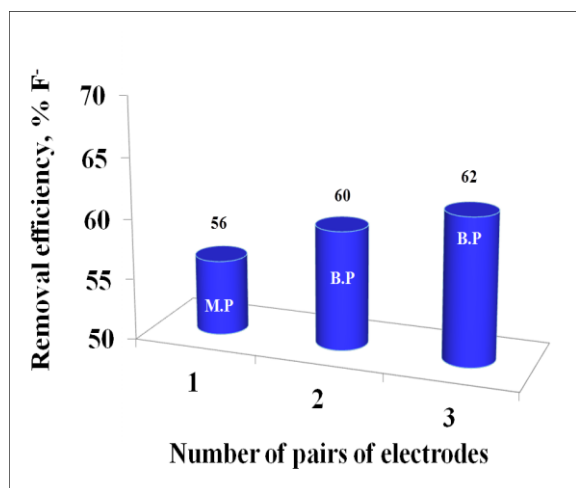


Fig. 10. Effect of the number of pair of electrodes and electrode connection mode on fluoride removal %F⁻, ($[F]_0 = 6 \text{ mg L}^{-1}$, pH = 6, $\sigma_i = 9 \text{ mS cm}^{-1}$, $J = 0,45 \text{ mA cm}^{-2}$, $d_{ic}=1 \text{ cm}$, and $t_{EC} = 20 \text{ min}$).

The results confirmed that the (B.P) connection with multiple electrodes can serve better fluoride removal than the (M.P) connection with two electrodes. In (B.P) connection, several electrochemical cells acted together for which higher surface area compared to that of (M.P) connection favored the adequate anodic oxidation. As a result, with the same current density applied for both kind of connection, the intensity is higher in the bipolar connection. It is also seen from Figure 10 that when the number of pairs of electrodes increases (2 - 3 pairs) and so the (S/V) ratio increases, fluoride removal increases. The reason of this observation is thought to be the workable rate of metal dissolution.

According to [13], the use of electrodes with large surface area is required and performance improvement has been achieved by using EC cells either with (M.P) electrodes or with (B.P) electrodes. However, to keep the EC system simple, the electrode plates are usually connected in (B.P) mode [14]. Experimental results showed that the high fluoride removal efficiency was obtained at $(S/V) = 22.4 \text{ m}^{-1}$ using 2 pairs of electrodes and (B.P) connection. The effect of the number of pairs of electrodes on energy consumption was also evaluated at 1, 2 and 3 pair(s). Our results displayed that energy consumption increased by increasing the number of pairs of electrodes as shown in Figure 11.

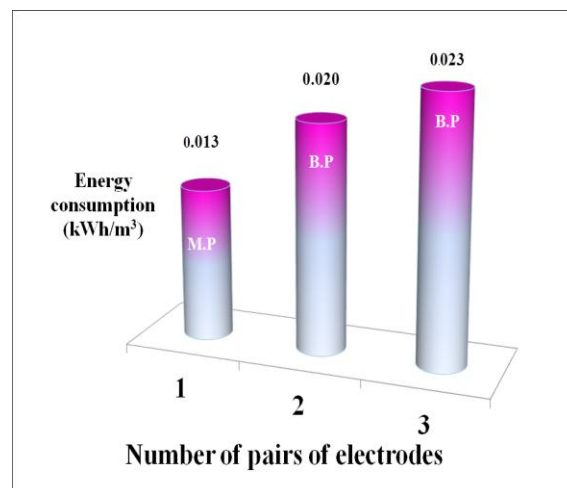


Fig. 11. Effect of the number of pair of electrodes and electrode connection mode on energy consumption, ($[F]_0 = 6 \text{ mg L}^{-1}$, pH = 6, $\sigma_i = 9 \text{ mS cm}^{-1}$, $J = 0,45 \text{ mA cm}^{-2}$, $d_{ic}=1 \text{ cm}$ and $t_{EC} = 20 \text{ min}$).

When the number of electrodes pairs increases, the number of electrode pair acting as single EC unit increases. Thus, the total cell voltage (that is the sum of the individual unit voltages) and the electrical energy consumed are increased. Accordingly, all EC experiments were conducted at $(S/V) = 22.4 \text{ m}^{-1}$ using 2 pairs of electrodes and (B.P) connection.

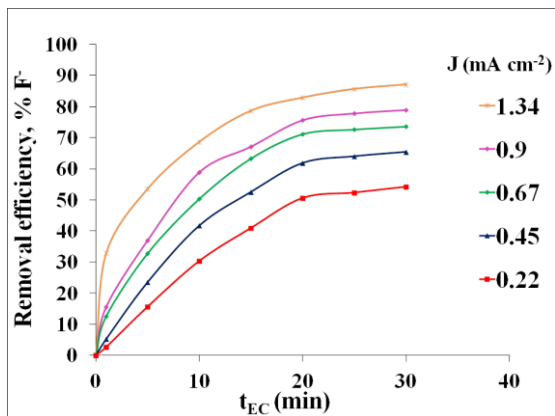
H. The effect of current density

Current density is one of the most critical operation parameters in electrocoagulation, having an integral effect on process efficiency. This parameter determines both the rate of electrochemical metal dosing to the water and the density of electrolytic bubble production [10].

The effect of current density on fluoride removal and energy consumption, was examined by varying current density value. The results obtained are shown graphically in Figures 6 and 7.

TABLE I. OPTIMAL CURRENT DENSITY AND OPTIMAL EC TIME FOR DIFFERENT FLUORIDE INITIAL CONCENTRATIONS.

$[F^-]_0$ (mg L ⁻¹)	$J_{optimal}$ (mA cm ⁻²)	t_{EC} (min)	$[F^-]_{res.}$ (mg L ⁻¹)	%F ⁻	W (kWh m ⁻³)
3	0.22	20	1.45	52.75	0.01
6	0.90	20	1.42	75.65	0.06
9	2.23	20	1.29	85.93	0.23
12	2.23	20	1.44	87.90	0.23

Fig. 12. Effect of current density on fluoride removal %F⁻, ($[F^-]_0 = 6 \text{ mg L}^{-1}$, pH = 6, $\sigma_i = 9 \text{ mS cm}^{-1}$ and $d_{ic} = 1 \text{ cm}$).

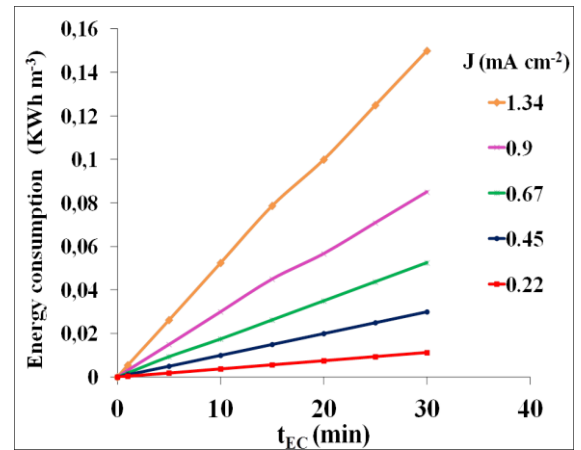
The appearance of the curves (Figure 12) shows a similar behavior: increases followed by a negligible variation. Removal fluoride efficiency tends to increase by increasing current density and EC time up to 20 min. However, with further EC time increase, defluoridation did not improve. Also obtained results displayed that an increase of current density notably reduces the treatment duration. This expected behavior is easily explained by the increase of coagulant and bubbles generation rate, resulting in a more efficient and faster removal, when the current is increased [15].

Generally an increase in current density causes the anodic oxidation to take place more readily, which in turn favors the formation of amorphous aluminium hydroxides species adequately in the vicinity of the electrode as well as in the bulk. Furthermore, this was also supported by the fact that with an increase in current density, the corrosion of the electrodes as well as the sludge formation also increases [5].

Although higher current density caused to solve more electrode material and remove more pollutant, this state was not desired for energy consumption. As a result of increasing current density, applied potential increased. Thus, energy consumption increased with increasing potential. High energy consumption with increasing current density and EC time was an expected result because energy consumption impressed linearly current density and EC time as seen in Eq. (2). The results obtained are shown graphically in Figure 13.

Although, it was apparent that with the time and the current density increases, the percentage of fluoride removal increases. However energy consumption increases. Thus, to choose the optimal current density and the optimal EC time, it was necessary to find a compromise between an economically appropriate energy consumption and an acceptable fluoride removal efficiency.

As shown in (Table 1), obtained results allow us to choose optimal conditions of current density and EC time for the different studied fluoride concentrations, to improve the fluoride removal efficiency and to minimize excessive energy consumption.

Fig. 13. Effect of current density on energy consumption, ($[F^-]_0 = 6 \text{ mg L}^{-1}$, pH = 6, $\sigma_i = 9 \text{ mS cm}^{-1}$ and $d_{ic} = 1 \text{ cm}$).

F. Experimental design methodology

We have investigated the influence of three main parameters: current density, initial fluoride concentration and initial pH using the experimental design methodology by means of factorial matrix (2^k) [16]. In these types of designs, variables (k) are set at two levels: low and high normalized as (-1) and (+1). With these designs, it was possible to calculate the average and the principle effects of each factors and their interaction.

The experimental response associated to a 2^k factorial design (for 3 variables) is represented by a linear polynomial model equation:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (10)$$

Where

Y: experimental response,

X_i : coded variable (-1 or +1),

b_i : estimation of the principal effect of the factor i for the response Y,

b_{ij} : estimation of interaction effect between factor i and j for the response Y.

The response investigated is the residual fluoride concentration. The coefficients of the equation model were calculated in the experimental field listed in Table II.

TABLE II. EXPERIMENTAL REGION INVESTIGATED FOR FLUORIDE REMOVAL BY EC

Coded variables (X_i)	Factors	Experimental field	
		Minimum level value	Maximum level value
X_1	J (mA cm ⁻²)	0.22	2.23
X_2	[F ⁻] ₀ (mg L ⁻¹)	3	12
X_3	pH	4	8

According to the results obtained, the coefficients of the polynomial model were calculated using the Nemrod-W Software:

$$Y = 2.15 - 1.13X_1 + 1.22X_2 + 0.15X_3 - 0.6X_1X_2 - 0.02X_1X_3 - 0.11X_2X_3 \quad (11)$$

The effects and interactions of the various investigated factors are represented in Fig. 14.

It was concluded that current density (J) has the highest effect. The effect of current density is negative, so it seems that residual fluoride concentration decreases when current density increases. Initial fluoride concentration is an important factor with a positive effect. So, residual fluoride concentration increases when initial fluoride concentration increases. The interaction among current density and initial fluoride concentration have an important effect with a negative effect. The initial pH has a positive effect but is not significant.

Pareto analysis [17] gives more significant information to interpret these results. In fact, this analysis calculates the percentage effect of each factor on the response, according to the following relation:

$$P_i = \frac{b_i^2}{\sum b_i^2} \times 100 \quad (i \neq 0) \quad (12)$$

Where b_i represent the estimation of the principal effect of the factor i for the response.

Figure 15 represents the Pareto graphic analysis.

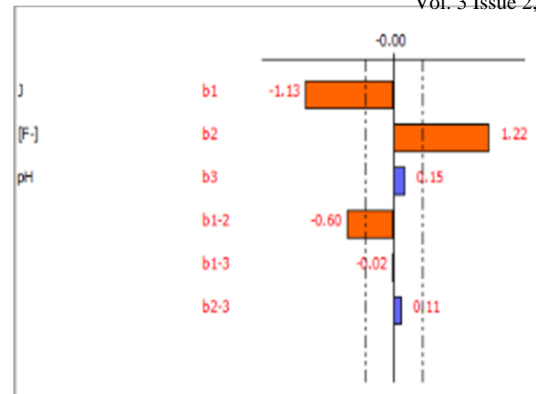


Fig. 14. Graphical analysis of the effect of: J, [F]₀ and pH on fluoride removal by EC.

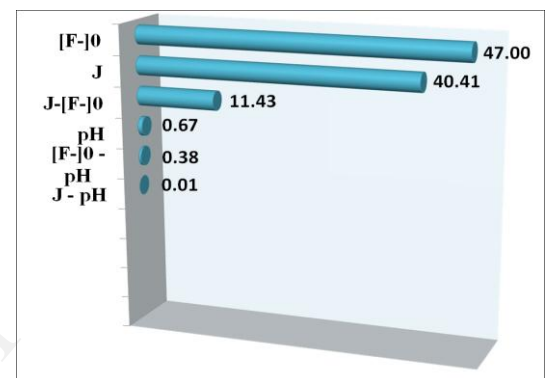


Fig. 15. Graphical Pareto analysis.

It shows that initial fluoride concentration and current density (J) the most determining factors on the removal of fluoride by EC; their effect is 87.41% on the investigated response. Therefore, more than 98% of the response are bringing by these two factors and their interaction. However, initial pH and the other interactions have a negligible effect, they represent a small degree lower than 1% of the response.

G. Application

In order to study the applicability of the process, experiments were conducted to determine the effectiveness of electrocoagulation treatment for fluoride removal from natural waters of south Tunisian. Before starting EC tests, were determined the main quality parameters of the water sample (Water Oued El Maleh-Gafsa). The results are summarized in Table III.

TABLE III. PHYSICO-CHEMICAL CHARACTERISTICS OF THE SAMPLE.

Parameter	Sample
Conductivity ($\mu\text{S cm}^{-1}$)	7970.00
Salinity (mg L^{-1})	6045.60
pH	7.40
Turbidity (NTU)	1.34
$[\text{Ca}^{2+}]$ (mg L^{-1})	240
$[\text{Mg}^{2+}]$ (mg L^{-1})	97.20
$[\text{F}^-]$ (mg L^{-1})	3.42

Physico-chemical characteristics of sample after treatment by electrocoagulation are presented in Table IV.

TABLE IV. PHYSICO-CHEMICAL CHARACTERISTICS OF THE SAMPLE AFTER TREATMENT BY EC.

Parameter	Sample
Conductivity ($\mu\text{S cm}^{-1}$)	7500.00
Salinity (mg L^{-1})	5689.00
pH	7.00
Turbidity (NTU)	0.40
$[\text{Ca}^{2+}]$ (mg L^{-1})	101.00
$[\text{Mg}^{2+}]$ (mg L^{-1})	40.16
$[\text{F}^-]$ (mg L^{-1})	1.34

The results shown in Tables 3 and 4 shows that the EC method could be an effective method for the defluorination of brackish water. Indeed, the concentration of fluoride ions decreases from 3.42 to 1.34 mg L^{-1} , corresponding to removal efficiency of 52% with low energy consumption of 0.012 kWh m^{-3} .

IV. CONCLUSION

The results of this study showed that EC process could be applied in the treatment of brackish water containing fluoride. Based on the results of experiments, the following conclusion may be obtained:

Optimization of the experimental conditions of fluoride removal showed that optimal fluoride removal was achieved for: $\text{pH}_i = 6$, $\sigma_i = 9 \text{ mS cm}^{-1}$, $d_{ie} = 1 \text{ cm}$, $(S/V) = 22.4 \text{ m}^{-1}$ and bipolar connection mode.

The statistical analysis of experimental design methodology showed that initial fluoride concentration and current density (J) had a considerable effect on fluoride removal by EC. Initial pH concentration was estimated as unimportant factor.

In order to study the applicability of the process, experiments were conducted to determine the effectiveness of EC treatment for defluorination of brackish water. Removal efficiency up to 52 % was achieved under optimal parameters and low energy consumption of 0.012 kWh m^{-3} . So it can be concluded that when EC process is used for fluoride removal from brackish water, it is possible to reach the limit recommended by WHO for fluoride concentration in drinking water, 1.5 mg L^{-1} .

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