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Electrocoagulation performance of industrial wastewater with high fluoride concentrations and characteristics of the sludge generated

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ABSTRACT

In the present work, the performance of electrocoagulation (EC), with aluminium sacrificial anode, in the treatment of fluoride containing synthetic photovoltaic wastewater, has been investigated. Experiments were performed for synthetic solutions in batch mode. The study focuses on the effect of following operational parameters: current density, charge loading, specific electrical energy consumption and anode consumption. Under the optimum conditions, initial pH of about 7, current density of 27.77 A/m^2, and inter-electrode distance of 1 cm, the fluoride removal was found to be 91.03%. The electricity consumption was found to be 5.5 kWh/kgF. X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy of X-rays and Fourier transform infrared spectroscopy analyses were used to characterize the residual EC by-product. The electrochemical treatment was found to be highly efficient and cost-effective compared with conventionally existing techniques.

Keywords: Electrocoagulation; Fluoride removal; Al electrode

1. Introduction

Photovoltaic solar cells manufacturers are continuously developing and improving production processes. Regardless of the technology used, a large amount of water is required and consequently, represents a major source of industrial *wastewater*. The wastewater from the production process must be treated in a way to recycle as much water as possible. Environmental and economic impacts associated with the photovoltaic systems are mainly due to hydrofluoric acid (HF) effluents generated during the various steps of fabrication [1]. In fact, wastewaters from PV industries (spent HF baths and waste rinse water) have high concentrations of fluoride. Several researches have demonstrated incontestably that waters bearing fluoride can cause sometimes-irreversible diseases in humans such as dental fluorosis or osteofluorosis, increasing the risk of fractures, hypothyroidism, acute nephritis and various lesions in the liver and heart [2]. Environmental authorities limit fluoride discharge levels to 15 mg/L [3]. It is revealed from the literature review that several technologies such as adsorption, membrane filtration, coagulation, oxidation, and biological treatment were used for the treatment of fluoride contaminated water [4]. All these technologies have their own limitations. Electrocoagulation (EC) process is one of the most promising technologies, gaining enough attention in recent years [5]. Electrocoagulation using aluminium anodes was successfully used for fluoride removal from pretreated acid waste [6].

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1.1. Fluoride removal by electrocoagulation process

Recent studies have demonstrated that the EC method using aluminum anodes is an attractive alternative for water defluoridation [2,7,8] because the EC method does not require chemical handling, it is easy to perform, and remarkably reduces the sludge volume and the required space. EC consists of generating coagulant species in situ by electrolytic oxidation of sacrificial anode materials triggered by electric current applied through the electrodes. The metal ions generated by electrochemical dissolution of a consumable anode spontaneously undergo hydrolysis in water, depending on the pH, forming various coagulant species including hydroxide precipitates (able to remove pollutants by adsorption/settling) and other ions metal species [9].

1.2. Theory of fluoride removal by the EC method

EC involves in-situ generation of coagulants by electrodissolution of aluminum electrodes [10]. Aluminum cations are generated at the anode and hydrogen gas is evolved at the cathode. Pollutants present in the aqueous medium are removed due to chemical precipitation or chemical and physical attachment to the coagulating ions being produced by the erosion of electrodes [11].

The electrochemical reactions at the electrodes are:

At the anode:

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3\ \mathrm{e}^- \tag{1}$$

At the cathode:

$$\mathrm{H_2O} + \mathrm{e}^- \rightarrow 1/2\ \mathrm{H_2} + \mathrm{OH}^- \tag{2}$$

Hydrolysis of Al ions:

$$\mathrm{Al}^{3+}\,(\mathrm{aq}) + 3\ \mathrm{H_2O} \rightarrow \mathrm{Al}\,(\mathrm{OH})_3 + 3\mathrm{H}^+\,(\mathrm{aq}) \tag{3}$$

Thus the highly absorbent aluminum hydroxide gel is formed in situ.

Generally, fluoride removal occurs due to three basic mechanisms [12]:

1. Adsorption on Al $(\mathrm{OH})_3$ particles:

$$\mathrm{Al_n(OH)_{3n}} + m.\mathrm{F}^- \rightarrow \mathrm{Al}_n\,\mathrm{F}_m\,(\mathrm{OH})_{3n-m} + m.\ \mathrm{OH}^- \tag{4}$$

2. Co-precipitation:

$$n.\ \mathrm{Al}\ (3n\text{-}m).\mathrm{OH}^- + m.\mathrm{F}^- \rightarrow \mathrm{Al}_n\mathrm{F}_m(\mathrm{OH})_{3n-m} \tag{5}$$

3. Fluoride attachment to the anode (physical attachment).

The particular objective of the present study was the investigation of the effect of important parameters in the EC process such as applied current, charge loading, specific electrical energy consumption (SEEC), and anode consumption on fluoride removal from rinsing water solutions generated by the photovoltaic processing industry. Furthermore, characterization by scanning electron microscopy (SEM)/energy dispersive X-ray analysis (EDAX), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) would provide key clues for removal mechanism.

2. Experimental

2.1. Apparatus and instruments

The EC experiments were carried out in a batch mode using about 1.5 L Plexiglas reactor (16.2 cm × 13.7 cm in dimension). Aluminium electrodes spaced by 1 cm were placed vertically in the reactor (Fig. 1) and were arranged in bipolar mode. Aluminium plate electrodes with dimensions of 10 cm × 10 cm × 0.2 cm (purity > 99.5%) were connected to a digital DC power supply (WG-INSTEK brand, model GPS-3030D 90W, 0-3A and 0-30V). The constant current was adjusted according to a desirable value. The total effective electrode surface area was 54 cm^2 and a gap of 2 cm was maintained between the bottom of the electrodes and the bottom of the cell to facilitate easy stirring. The solution in the reactor was constantly stirred at 300 rpm.

2.3. Experimental procedure

In order to simulate the photovoltaic wastewater, the desired concentrations of F^- solution were prepared by dissolving 1 N HF stock solution in deionized water and then reacted with lime ($\mathrm{Ca(OH)_2}$). Before each run, electrodes rubbed with sand paper and then dipped in dilute chloride acid solution and distilled water for surface cleaning. After cleaning, electrodes were weighted. The electrodes were placed into the EC reactor. The range of current values varies from 75 to 200 mA. The current was held constant at desired values for each run and the experiment was started. Changes of voltage on the DC power supply during the experiment were recorded. Sodium chloride was used as a supporting electrolyte and the pH was adjusted by adding sodium hydroxide (1 N) or sulfuric acid (1 N). The samples taken from the EC reactor at the different operating times were filtered using a 0.45 m filter and final pH, concentrations of F, were measured. At the end of the experiment, the electrodes were washed thoroughly with water to remove

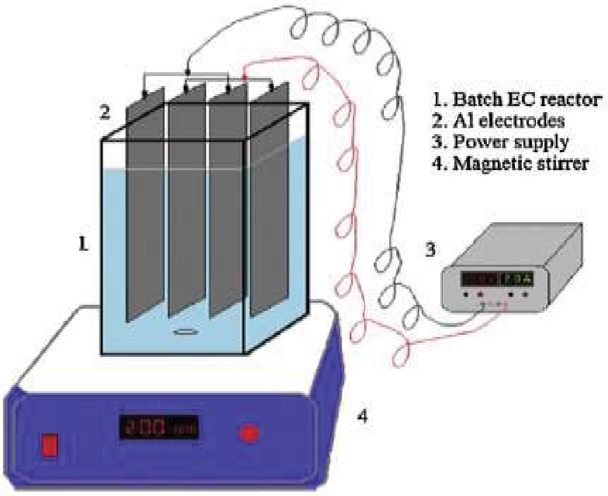


Fig. 1. Experimental setup used in the EC process.

any solid residues on the surfaces dried and reweighed. The total time duration of electrolysis was 120 min. The sludge generated after the EC process was filtrated by a Whatman N° 46 filter paper, and dried in the oven at 105°C for 24 h, before the sludge analysis. Amounts of the sludge generated in the EC were 0.068 kg/L. All experiments were carried out at room temperature. The experimental conditions considered in this study are listed in Table 1.

2.4. Analytical procedures

A combined selective ion electrode (sensION1 from HANNA HI 4110) was used to determine the fluoride concentration according to the ionometric standard method [13]. The TISAB II at pH 5.5 containing CDTA was added to samples in order to maintain constant ionic strength and to prevent the interference from Al^{3+} and Ca^{2+} cations.

The pH values were determined by using SensION1 pH meter HANNA Instruments HI8424. The analysis of the metal species present in the precipitate was carried out with an ultra-high-resolution field-effect scanning electron microscope: JEOL JSM-7610F Plus coupled to an SDD-type EDA-X, USA) energy dispersive X-ray spectrometer BRUKER Quanta X Flash 6/10 (Germany). The SEM images were taken at different energies (15 kV).

The FTIR analysis of the flocs was carried out in a Perkin-Elmer Spectrum GX FTIR spectrometer using an EasiDiff diffuse reflectance accessory. Spectra were acquired by averaging 64 scans over the range 400–4,000 cm^{-1} at 4 cm^{-1} resolution. Thermo Scientific OMNIC™ (USA) research software was used to control the FTIR spectrometer and process resultant spectra. The flocs samples were prepared using potassium bromide.

XRD analysis has the Philips (The Netherlands) "X'PERT PRO MPD" diffractometer in q-q mode (Bragg–Brentano configuration, equipped with a vertical 240 mm radius goniometer and equipped with a ray tube X with copper anticathode. The interfaced detector is of the PIXcel-1D type. The type of sample holder is a spinner. Spectrum processing was obtained by "X'Pert HighScore Plus" software.

3. Results and discussion

3.1. Effect of current density

Current density is a measure of the amount of current passed through unit cross-section area. Current density plays an important role in removal of fluoride in the electrocoagulation process, as it determines the rate of coagulant dosage, bubble production, size and growth of flocs, which influence the removal efficiency of electrocoagulation [14]. Moreover, it will strongly influence the solution mixing and the mass transfer at the electrodes. Thus, this parameter is expected to have a significant impact on fluoride removal efficiencies [8]. In the present study, the applied current was varied from a considerable low value of 0.05 A (9.25 A/m^2) to the upper value of 0.20 A (37.03 A/m^2). The time of electrolysis was kept constant at 120 min. The samples were collected at an interval of 10 min and residual fluoride was measured. Fig. 2 illustrates that the increase in current results in a decrease in residual fluoride concentration.

Table 1
Operating conditions

Parameters values	Values
Fluoride (mg/L)	100
pH	7
Number of electrode	3
Inter electrode distance (cm)	1
Applied current (mA)	50–200
Electrolyse time (min)	120
Sedimentation (h)	3

When the current varies between 100 and 200 mA, the final concentration of fluoride varies between 8.72 and 1.14 mg/L, respectively. Lower the applied current, lower is the aluminium generated and hence fluoride reduction is low. According to Faraday's law, the increase in current density allows a higher dosage of coagulant per unit of time [15]. However, very high current values may negatively affect the EC efficiency. For instance, secondary reactions may occur and can reverse the charge of the colloids and further disperse them leading thereby to a decrease of the coagulant efficiency and to a reduction of the electrode lifetime [9].

Chalbi and Ben Mansour [16], and Aoudj et al. [17] found that the percentage of elimination/reduction increases with increasing current intensity to an optimal value, but a further increase in current reduces the elimination/reduction efficiency. As a result, an appropriate selection of current density needs to take account for various factors such as treatment time, pH, SEEC to ensure that fluoride removal in EC process is operated at the optimum conditions. To operate the EC system for a long period without maintenance, the current density is suggested to be between 20 and 25 A/m^2 [9]. In this study, the higher removal fluoride efficiency was obtained for applied current of 0.15 and 0.20 A

3.2. Effect of charge loading

The quality of EC effluent depends on the amount of coagulant produced (mg) or applied charge loading. Some researchers [18,19] to assess the removal of fluoride from water have also used charge loading. Charge loading is

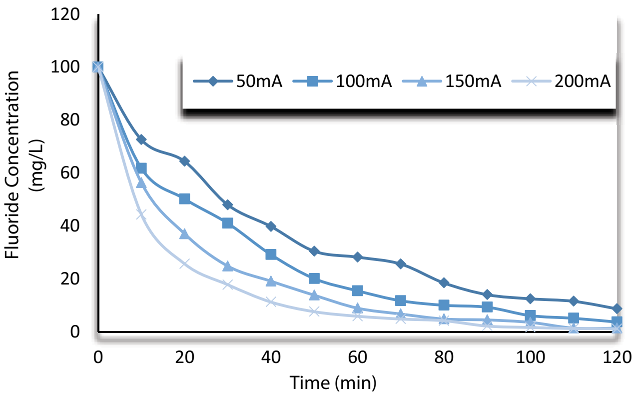


Fig. 2. Effect of current intensity on the removal of fluoride.

defined as the charge transferred in electrochemical reaction for a given amount of water treated and is calculated by using the equation:

$$Q_{(\mathrm{C/L})} = I \times \frac{t_{(\mathrm{EC})}}{v} \quad (5)$$

where Q is the charge loading in C/L, I is the applied current in A, t is the treatment time in s, and V is the volume of water treated in L. Effect of different charge loading on fluoride removal was investigated for two applied current values (0:15 and 0:20 A) and for the same reaction time. The results are illustrated in Fig. 3. These results can be explained by Faraday's law, which states that the amount of metal dissolved electrochemically is proportional to the charge loading [20]. When the charge loading is low, the dosing of aluminium is not sufficient. As a result, a small amount of Al $(OH)_3$ flocs are formed which does not remove the fluoride effectively.

It can be observed from Fig. 3a that as the charge loading is increased loading from 60 to 600 C/L, the residual fluoride decreased from 56.36 to 4.87 mg/L at an applied current of 0.15 A and initial fluoride concentration of 100 mg/L. With increase in charge loading, the dosage of aluminum increased, thereby increasing the floc formation. Hence, more fluoride can be adsorbed onto the flocs and fluoride removal increased. Significant increase in fluoride removal can be observed in the initial stages. Similarly, at an applied current of 0.20 A significant decrease was observed, crossing which no considerable enhancement in fluoride removal can be seen. Zhu et al. [21] and Chen et al. [22] obtained similar trends. The results indicated that a critical charge loading is required and once that value is reached, no significant enhancement in fluoride removal can be observed.

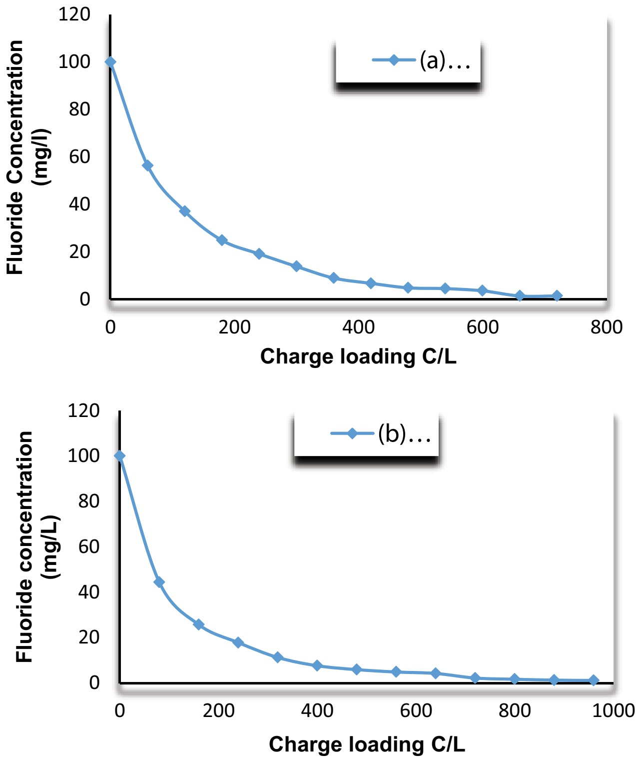


Fig. 3. Effect of charge loading on fluoride removal: (a) 0.15 A, (b) 0.20 A.

3.3. Anode consumption

Applied current and electrolysis time are the two major operating parameters in EC process, which determines the dissolution of aluminium in the reactor. Aluminium dissolution can be calculated using Faraday's Law. Faraday's Law of electrolysis states that for a given quantity of D.C electricity (electric charge), the mass of an elemental material altered at an electrode is directly proportional to the element's equivalent weight. In the context of the present study, Faraday's Law determines aluminium dissolution from the electrode [23]. The coagulant generation is described by the following equation:

$$\mathrm{Al}_{\mathrm{th}} = \frac{M \times I \times t}{Z \times F} \quad (6)$$

where $\mathrm{Al}_{\mathrm{th}}$ is the mass of the metal dissolved (g), I is the current (A), t is the time of EC process (s), M is the molecular weight of the metal (g/mole), Z is the number of electrons involved in the redox reaction (for the aluminum $n = 3$), and F is Faraday's constant (96,485 C/mole).

In Fig. 4 relation between theoretical aluminum dissolution, residual fluoride and electrolysis time has been shown. It can be observed that as the dose increases the removal efficiency increases up to a certain extent, after which the change in efficiency is marginal. Therefore, the only required extent of treatment must be given to restricting the unnecessary coagulant to enter the reactor.

3.4. SEM characterization of electrodes

Magnified SEM images of the unused electrode, anode, and cathode, before and after, electrocoagulation of fluoride electrolyte was obtained to compare the texture of the electrode's surface. Fig. 5 shows that the surface of the anode

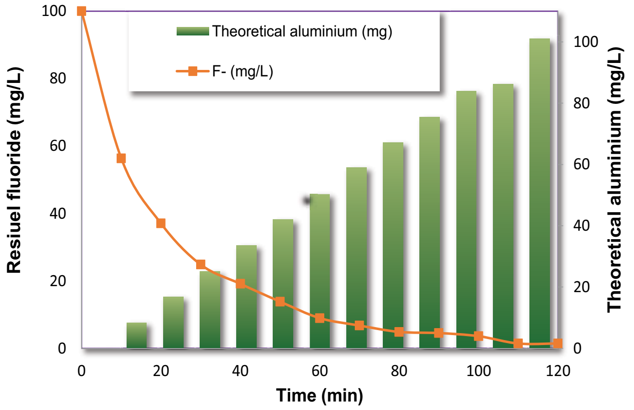


Fig. 4. Effect of electrolysis time and applied current on theoretical aluminum and residual fluoride (pH 7, $I = 0.15$ A).

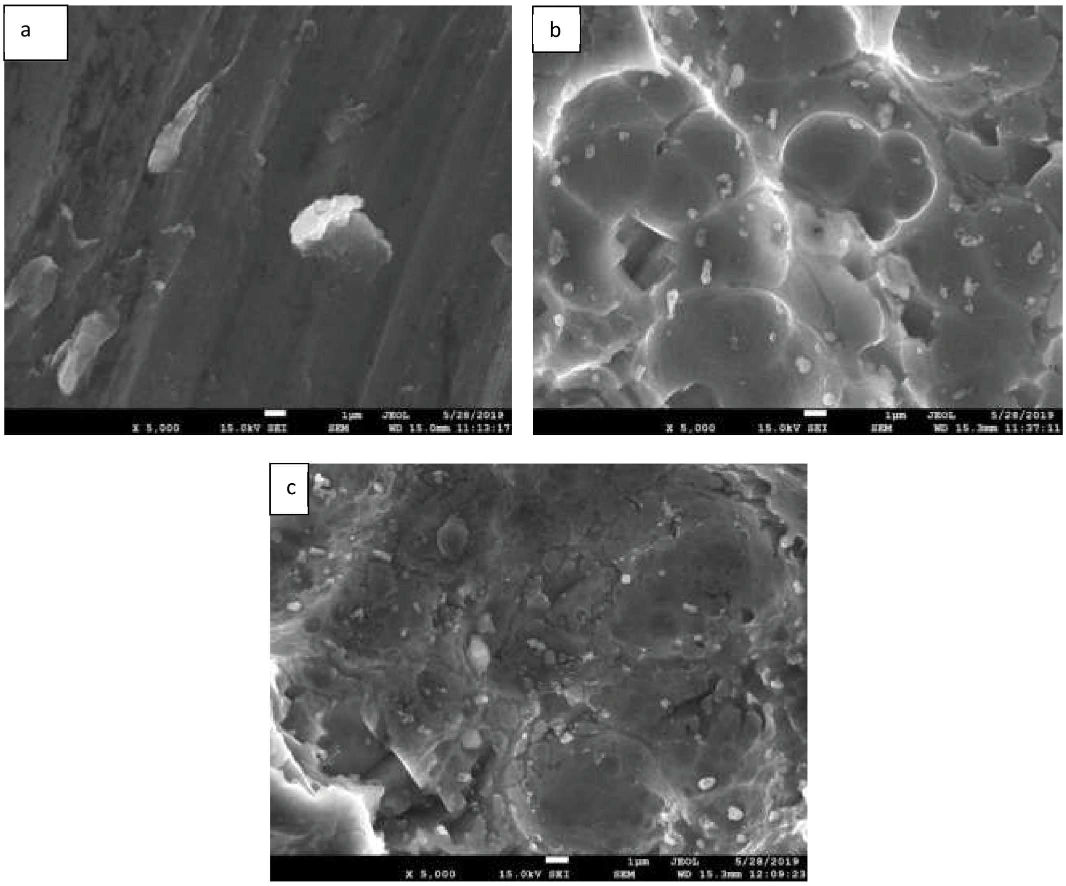


Fig. 5. SEM images of Al electrode before EC (a), anode (b) and cathode (c) after EC.

before the electrocoagulation process was uniform, except for small dents, which could have occurred due to the polishing of the metal during the electrode shaping process. While for the anode and the cathode (Figs. 5b and c), there are signs of craters corresponding to pitting corrosion. The surface of the anode has become rough, spongy and macroporous after a series of experiments. This state could be attributed to the consumption of anodic material at the active sites where the dissolution of the anode causes the generation of aluminum hydroxides [11].

3.5. Specific electrical energy consumption

SEEC controls energy input and aluminium dissolution in EC process and hence it is an important parameter of concern. SEEC is defined as energy per unit mass of fluoride removed and calculated by Eqs. (7) and (8).

$$\text{SEEC} = \frac{\text{Energy consumed}}{\text{Fluoride removed}} \tag{7}$$

$$\text{SEEC}\left(\text{Kwh/KgF}\right) = \frac{U \times I \times t}{\left(Ft - Fr\right) \times V} \tag{8}$$

where U is the voltage in V, I is the applied current in A, t is the electrolysis time in min, V is the volume (L), F_t is the total fluoride present in the solution in mg/L, F_r is the fluoride removed from the solution after EC treatment in g/L.

In the present study, SEEC was calculated for an applied current of 0.15 and 0.20 A. The results are shown in Fig. 6. It can be observed that SEEC increases with an increase in time for a constant current. It can be seen in Fig. 6a that SEEC increases from 1.909 to 5.5 kWh/kg when the time is increased from 10 to 60 min; at an applied current of 0.15 A. At 90 min of electrolysis time, SEEC increases from 7.85 to 20.52 kWh/kg when the applied current was increased from 0.15 to 0.20 A, we observed that SEEC increased significantly.

When high current densities are applied, the removal of fluoride increases. However, it should be noted that more sludge is also produced because of the high dissolution rate of the aluminum anode electrode, which will increase the cost of the treatment process. For maintaining the cost evaluation of the process, energy input (I, t) should be minimized for bringing fluoride within the permissible limit. From these results, we can deduce that the applied current of 0.15 A provides the optimal conditions for removal efficiency of fluoride ions.

4. Characteristics of sludge

In order to study the mechanism of fluoride removal during the use of aluminum salt, the composition of the produced sludge was studied using different characterization methods such as SEM/EDAX, XRD and FTIR. The sludge production in the EC process was proportional to current density and operating time including characteristics of wastewater, settling solids and matter destabilized by coagulation and concentration flocculent as well [24].

4.1. Scanning electron microscopy and energy dispersive X-ray

The SEM images (a) and (b) of Fig. 7 show the morphology of the precipitate produced by the electrocoagulation process for current densities of 0.15 A (27.77 A/m^2) and 0.20 A (37.03 A/m^2) so as to evaluate the structural features and elemental composition of sludge.

Fig. 7a shows agglomerated grains of different sizes, which mainly attributed to fluorine and crystallized grains attributed to aluminum. By increasing the density from 27.77 to 37.77 A/m^2 (Fig. 7b), the morphology of the sludge has completely changed and this is due to the difference in the amount of aluminum dissolved during the process. The elemental analysis by EDX (Fig. 8) confirmed the presence of F removed (56.42 at. %, i = 27.77 A/m^2) from the sample solution. Other elements detected in the sludge come from adsorption of conducting electrolyte, chemicals used in the experiments and scrap impurities of Al electrodes [25].

4.2. Fourier transform infrared spectroscopy

The electro co-precipitated sludge generated during electrocoagulation was analyzed using the FTIR spectrometer. FTIR analysis ranged from wave number 4,000–450 cm^{-1} was performed to analyze the chemical bonds of the flocs, Fig. 9. The infrared spectrum analysis of the defluoridation process showed two bands at 3,500 and 3,000 cm^{-1}, which correspond most likely to H–O–H stretching vibrations [26].

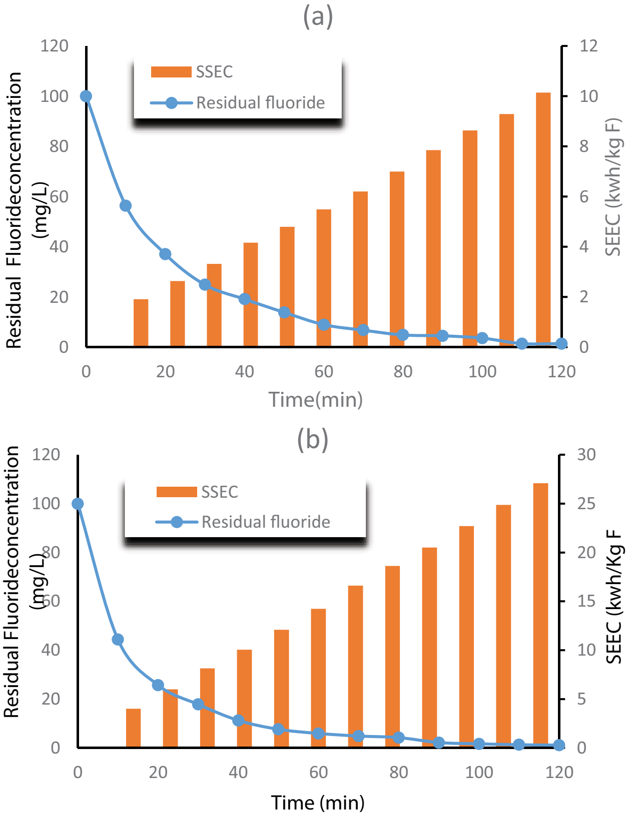
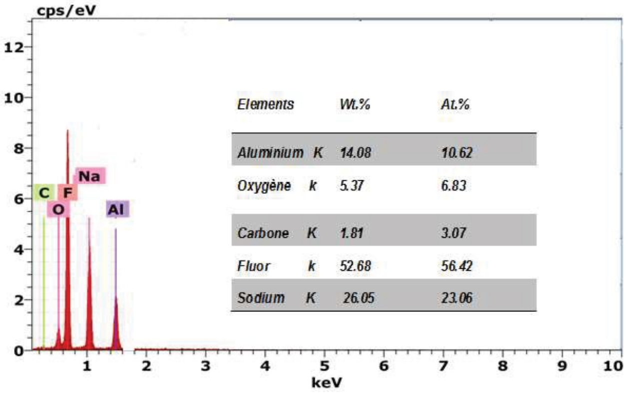


Fig. 6. Effect of electrolysis time and applied current on SEEC for different applied current (a) 0.15 and (b) 0.20 A.



Elements		Wt.%	At.%
Aluminium	K	14.08	10.62
Oxygène	k	5.37	6.83
Carbone	K	1.81	3.07
Fluor	k	52.68	56.42
Sodium	K	26.05	23.06

Fig. 8. EDAX results of sludge produced in EC process (I = 0.15 A, $[F^-]_0$ = 100 mg L^{-1}, pH = 7).

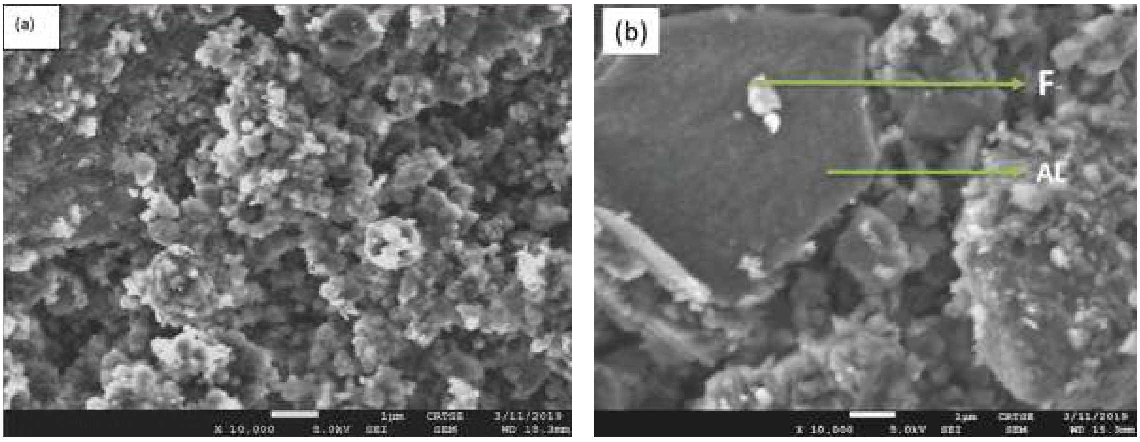


Fig. 7. SEM visualization of sludge after 120 min of EC (a) 0.15 and (b) 0.20 A.

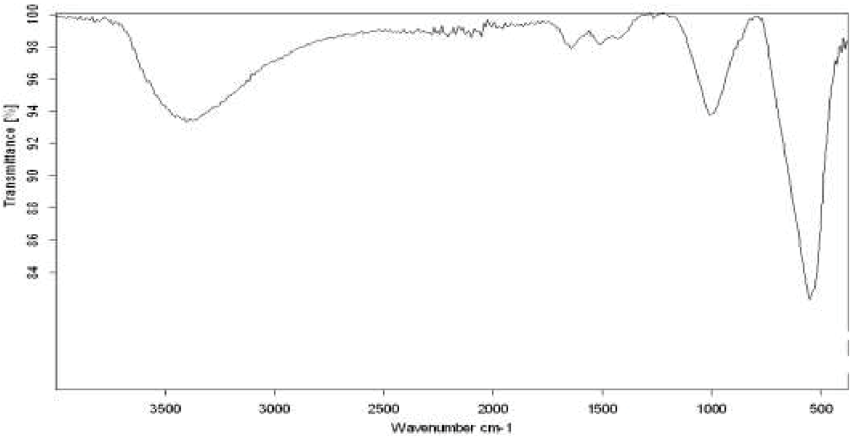


Fig. 9. FTIR results of sludge produced in EC process ($I = 0.15$ A, $[F^-]_0 = 100$ mg L^{-1}, pH = 7).

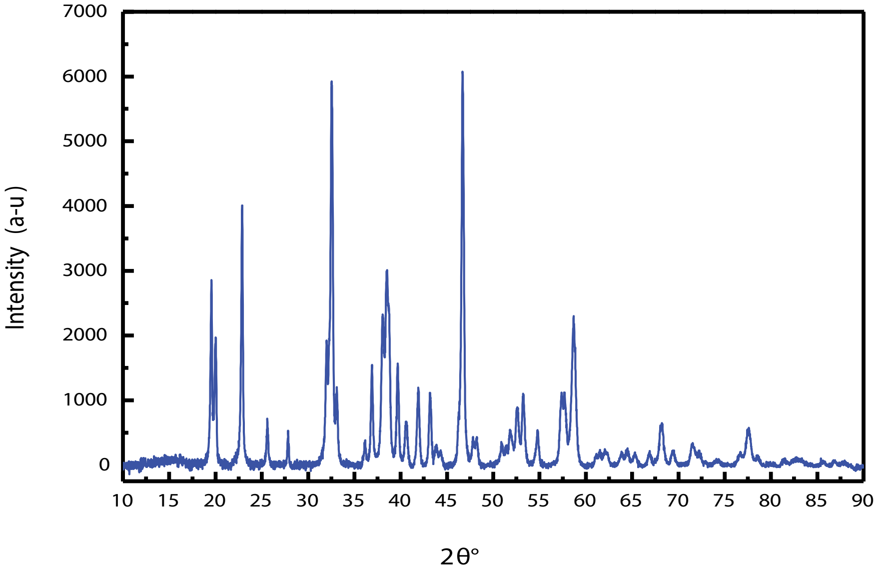


Fig. 10. XRD diagram for aluminum sludge produced in the electrocoagulation process ($I = 0.15$ A, $[F^-]_0 = 100$ mg L^{-1}, pH = 7).

The stretching around 590 cm^{-1} corresponded to F–Al–F bend of AlF_3 [10]. The peaks in the 700–1,300 cm^{-1} region corresponded to the stretching and bending modes of Al–O [2]. The peak located at 1,750 cm^{-1} is likely attributed to the Na–F bonding [26]. The peak located at 1,006 cm^{-1} is attributed to Al–O–Na [27]. The FTIR analysis confirms that F replaces OH group from $Al(OH)_3$ flocs, and precipitated in the reactor, which is in agreement with that obtained by Aoudj et al. [28].

4.3. X-ray diffraction

The XRD pattern of aluminum electrode coagulant as presented in Fig. 10. The strongest peaks identified in the XRD spectrum were sodium aluminium fluoride ($Na_3(AlF_6)$), some peaks can be attributed to aluminium fluoride hydrate ($AlF_3(H_2O)_3$). The formation of these compounds suggests the removal mechanism of fluoride in the EC process. It shows that the fluoride may occur in solids particles such as aluminium fluoride hydroxide complexes. These observations confirm the hypotheses on the adsorption and complexation mechanisms of defluorination [25,29,30].

5. Conclusion

The experimental results demonstrate that increasing the current density and the contact time resulted in an enhanced reduction of the fluoride concentration. Applied current and electrolysis time are the major parameters which govern the EC process; however they have their limitations. Moreover at high charge loading conditions the utility of electro-generated Al ions is much low. Under conditions of pH 7 and electrode number 3, the intensity of 0.15 A offered the best results for SEEC of 5.5 kWh/kgF. Increase in applied current leads to increased energy consumption and increased aluminium dissolution, which affect the economics of the process and might also end up in more residual aluminium at the end of the treatment process. Therefore, while running the EC process, the selection of these two parameters requires attention and a tradeoff has to be made between them. Additionally, it was seen from the experiments that 50 min EC was enough for reaching the standard limits to the destined environment for fluoride discharge in Algeria (limits discharge 15 mg/L).

SEM analyses were performed to evaluate the morphology of the flocs obtained from the EC process show agglomerated grains of different sizes at 0.15 A. EDAX analysis confirms the presence of Al, F, O, and Na elements, which indicates that the aluminum flocs entrap the fluoride. FTIR analyses suggested that fluoride removal by EC was carried out by means of a chemical substitution in which F replaced OH^- group from de Al $(OH)_3$ flocs producing Al(OH)3xFx. The XRD analysis of the composition of the dried sludge obtained by EC process shows the formation of sodium aluminium fluoride ($Na_3(AlF_6)$). Furthermore, the analysis of XRD and FTIR data together with SEM/EDAX suggests that adsorption and complexation are the dominant removal mechanisms.

The results of this study indicate that current density was the key operating parameter which strongly affects EC performance, in terms of the removal efficiency and energy consumption. EC process is a promising method for effectively removing F^- from synthetic photovoltaic wastewater.

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