



## Study on the treatment of photovoltaic wastewater using electrocoagulation: Fluoride removal with aluminium electrodes—Characteristics of products

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### ABSTRACT

In this work, treatment of synthetic fluoride-containing solutions by electrocoagulation method using aluminium electrodes has been studied. Electrocoagulation was investigated for applied potential (10–30 V), electrolysis time and supporting electrolyte (NaCl) concentration (0–100 mg/L). The results showed that with increasing applied potential and electrolysis time, the Al<sup>3+</sup> dosage increases, and thereby favouring the fluoride ions removal. It was also observed that defluoridation is dependant on the concentration of supporting electrolyte. Finally, X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy of X-rays and Fourier transform infrared spectroscopy were used to characterize the solid products formed by aluminium electrodes during the EC process.

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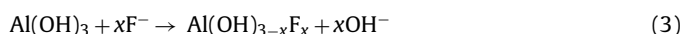
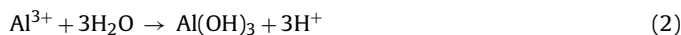
### 1. Introduction

Photovoltaic (PV) energy conversion is increasingly regarded as a technology which may contribute to the world energy supply in a way that is compatible with the concept of sustainable development. However, to ensure that PV energy can indeed fulfil this expectation, a careful consideration of potential environmental risks of PV energy conversion is necessary [1].

PV manufacturing process, which requires extremely high precision, generates both conventional and hazardous wastes. The management of waste has become an important issue in the industry as a result of stringent environmental regulation and possible liability. Among varieties of pollutants, hydrofluoric acid (HF) is a major concern. It is used extensively in PV manufacturing for wafer etching and quartz cleaning operations [2]. Fluoride concentrations of 500–2000 mg/L are found in typical wastewater of local PV industry [3]. Fluoride contamination in certain aquatic systems worldwide has caused health concern. Due to its high toxicity, industrial wastewater containing fluoride is strictly regulated. In Algeria, the discharge standard is of 15 mg/L from wastewater treatment plant [4].

Various treatment technologies, based on the principle of precipitation, ion exchange, membrane and adsorption process have been proposed and are tested for removal efficiency of excess of fluoride from drinking water as well as industrial effluents [5].

In recent years, there is growing interest in electrocoagulation (EC). This technique can be used to treat effectively restaurant wastewater [6], textile wastewater [7], electroplating wastewater [8], and fluoride-containing wastewater [9,10]. It has also proven its good efficiency for drinking water defluoridation [11–13]. EC technique uses a direct current source between metal electrodes immersed in polluted water. The electrical current causes the dissolution of metal electrodes commonly iron or aluminium into wastewater. The metal ions, at an appropriate pH, can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants [14]. EC is attractive in that no contaminants are introduced and beneficial contents present in raw water can be remained during defluoridation. In the case of aluminium electrodes, the main reactions involved are as follows:



Defluoridation is achieved by forming Al(OH)<sub>3-x</sub>F<sub>x</sub>. The fine hydrogen gas bubbles generated at the cathode can enhance F<sup>-</sup> mass transfer and float the Al(OH)<sub>3-x</sub>F<sub>x</sub> flocs to the top of the

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EC unit. Since fluoride in the water is transferred to  $\text{Al}(\text{OH})_{3-x}\text{F}_x$ , the latter must be separated effectively from the water in order to achieve effective defluoridation [13].

This study mainly focused on the effects of cell voltage, electrolysis time and supporting electrolyte on EC performance for the removal of fluoride from synthetic solutions. The characterization of the EC by-products using powder X-ray diffraction (PXRD), scanning electron microscopy (SEM)/energy dispersive analysis of X-rays (EDAX), and Fourier transform infrared (FT-IR) were also done.

## 2. Experimental

### 2.1. Materials and methods

The EC experimental apparatus is shown in Fig. 1. The electrolytic cell was a 1 L parallelepipedic plexiglas reactor which was equipped with an external water jacket for temperature control. A steady temperature of 293 K was maintained for all test runs. Aluminium (Al) plates (114 mm  $L \times$  140 mm  $W$ ) were used as anode/cathode pair. The aluminium electrodes were installed vertically, and connected in a bipolar mode. The electrodes were dipped in the PV synthetic wastewater to a depth of 10 cm and were situated 1 cm apart. The effective area of the electrode pair was 80 cm<sup>2</sup>. The DC power supply was a P. Fontaine MC 3030C generator. Cell potential was controlled by a voltmeter. The studied solution is injected into the electrochemical reactor cell by means of the centrifugal Fontaine M7 feed pump, which allows flow rates of up to 460 L h<sup>-1</sup> and maintains well mixing of the solution during EC run.

Furthermore, the previous results showed that the defluoridation process is more efficient when pH is kept constant between 6 and 8 during experiments. So, the pH was kept constant in this range for each run.

Wastewater samples were taken every 10 min for water quality measurements. Remaining volume of the treated PV synthetic solutions was put in the sludge settling column. A sludge settling test run lasted up to 3 h.

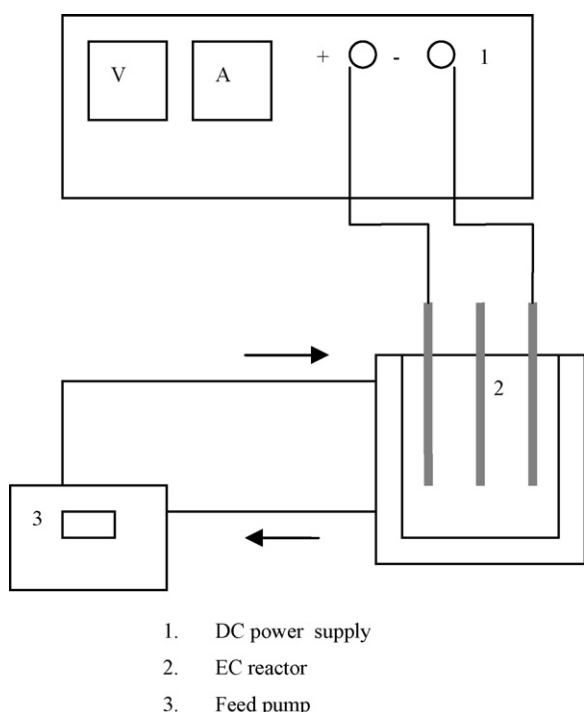


Fig. 1. Diagram of the experimental setup.

### 2.2. Chemicals

The testing water solution was prepared artificially by dissolving a proper amount of NaF and supporting electrolyte NaCl, into deionized water to simulate the photovoltaic wastewater.

### 2.3. Chemical analysis

A selective ion sensor electrode [PF4L from Tacussel (Lyon, France)] was used to determine the fluoride concentration, according to the standard method given by American Public Health Association [15]. To prevent the interference from other ions ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$ ), TISAB II buffer solution containing CDTA (cyclohexylenediaminetetraacetic acid, Orion Research Inc.) was added to the samples.

Environmental SEM Philips (type ESEM XL30 FEG) combined with EDAX are used to characterize the sludge. SEM pictures were taken at 10 kV at various magnifications.

The PXRD analysis of the EC by-products was carried out with a Bruker AXS D4 Endeavor diffractometer operating with a Cu  $K_{\alpha}$  radiation source and filtered with a graphic monochromator ( $\lambda = 1.5406 \text{ \AA}$ ).

Infrared analysis was carried out with Perkin Elmer paragon 1000 spectrum RX and the results were obtained with OMNIC software.

## 3. Results and discussion

### 3.1. Effect of applied potential

It is known that in EC, applied cell potential determines the coagulant amount and also adjusts the rate and size of the bubble production and hence affects the growth of flocs. To investigate the effect of applied potential on the efficiency of fluoride removal, electrocoagulation process was carried out using various voltages (10, 20, and 30 V). The effect of voltage on the fluoride removal is shown in Fig. 2. With increase in voltage from 10 to 30 V the percentage amount of fluoride removed also increased. For instance after 80 min of treatment, residual fluoride concentration is 9.5 mg/L for applied voltage of 30 V, whereas for 20 and 10 V it is 10.3 and 14.2 mg/L respectively. This is mainly due to insufficient amount of electric power at lower voltages to produce  $\text{Al}(\text{OH})_{3-x}\text{F}_x$  species and gas bubbles responsible for defluoridation.

### 3.2. Effect of electrolysis time

Electrolysis time influences the treatment efficiency in the electrochemical process. Reaction time determines the rate of production of  $\text{Al}^{3+}$  ions from aluminium electrodes. The pollutant

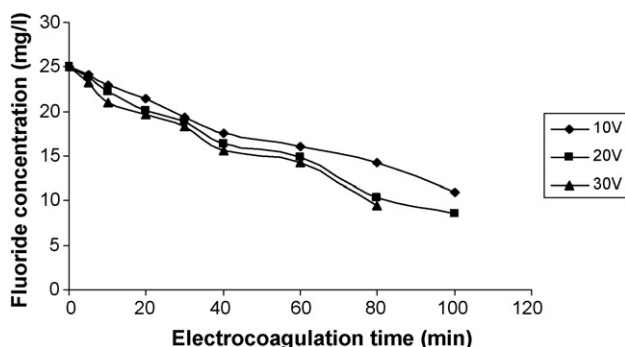
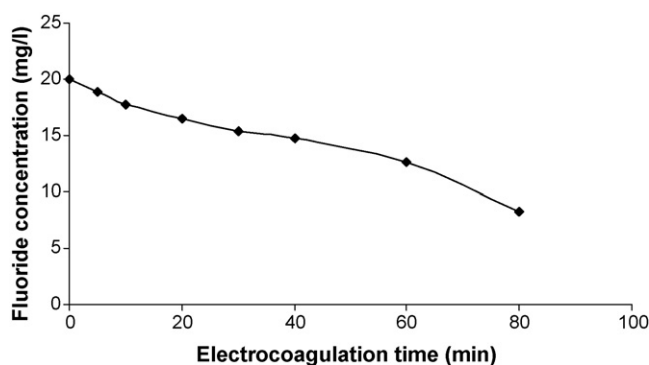


Fig. 2. Fluoride residual concentration as a function of applied potential. Initial fluoride concentration, 25 mg/L;  $T$ , 20 °C; supporting electrolyte concentration, 0 mg/L.



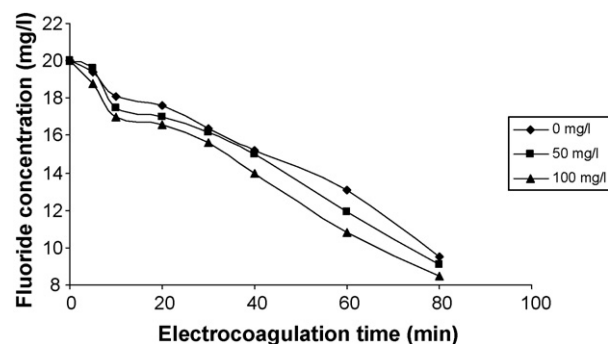
**Fig. 3.** Fluoride residual concentration as a function of electrolysis time. Initial fluoride concentration, 20 mg/L;  $T$ , 20 °C; supporting electrolyte concentration, 100 mg/L; applied potential, 20 V.

removal efficiency depends directly on the concentration of metal ions and hydroxyl produced on the electrodes [16]. During electrolysis, the positive electrode undergoes anodic reactions. The released ions neutralize the pollutant particle charges and thereby initiate coagulation. When the electrolysis period increases, the concentration of ions and their hydroxide flocs increases [17]. Accordingly, it can be seen from Fig. 3 that with increasing electrolysis time, the fluoride removal efficiency increased. In fact, an increase in the time of electrolysis from 5 to 80 min yields to a decrease in the fluoride concentration from 18.9 to 8.3 mg/L. It should be noted that, under these conditions, synthetic fluorinated solution reached the concentration recommended by the discharge standards.

### 3.3. Effect of supporting electrolyte

It is known that, in electrochemical process, the presence of supporting salt in the solution affects the current efficiency, cell voltage and consumption of electrical energy [16]. The supporting electrolyte effect is studied by using NaCl. Three concentrations were used: 0, 50 and 100 mg/L. Fig. 4 illustrates fluoride concentration dependence on the supporting electrolyte dose. It can be said that the addition of NaCl clearly enhances the ion removal. The results show that when the salinity of the effluent is increased from 0 to 100 mg/L, the amount of fluoride decreased from 13.08 to 10.8 mg/L.

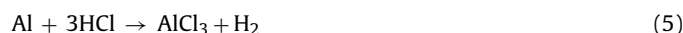
Similar results were reported by Modirshahla et al. [18] and Daneshvar et al. [19]. They found that an increase in



**Fig. 4.** Fluoride residual concentration as a function of supporting electrolyte concentration. Initial fluoride concentration, 20 mg/L;  $T$ , 20 °C; applied potential, 30 V.

NaCl concentration leads to an increase in pollutant removal efficiency.

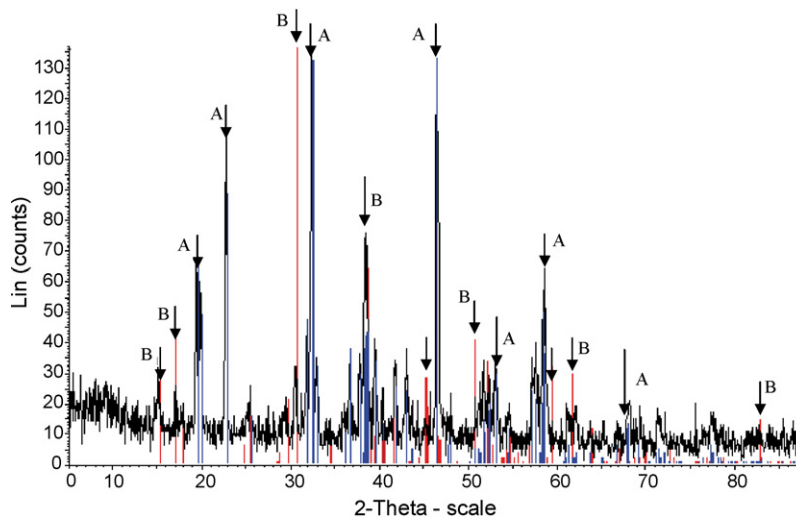
In our conditions, this increase in the defluoridation efficiency is probably attributed to the “pitting corrosion” phenomenon at the EC electrode due to the presence of chloride ions. The “pitting corrosion” can produce more aluminium hydroxide flocs, as shown in reactions (5) and (6). This leads to an improvement in the fluoride removal process [11].



In addition, the other benefit of increasing the salt concentration is the raising of the electrical conductivity of the water which causes more current passing through the circuit under the same applied potential.

### 3.4. Sludge characterization

Knowing the sludge composition and material crystalline structures would provide valuable information regarding EC fluoride removal fundamental mechanisms. In this study, powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) coupled with energy dispersive analysis of X-rays (EDAX), and Fourier transform infrared spectroscopy (FT-IR) were used to characterize the solid products formed at aluminium electrodes during the EC process.



**Fig. 5.** XRD diagram for aluminium sludge produced in the electrochemical process (cryolite: A, sodium aluminium fluoride: B).

### 3.4.1. XRD characterization of electrode by-products

The XRD analysis was carried out to identify the morphological structure and the extent of crystallinity of the aluminium sludge. Fig. 5 shows a diffractogram of the electrode by-product after defluoridation. It showed very broad and shallow diffraction peaks demonstrating most likely amorphous/poorly crystalline phases for aluminium hydroxide/oxyhydroxides.

From FT-IR analysis of the Al electrode by-product, it can be concluded that the chemical speciation of this amorphous phase can be aluminium hydroxide and/or aluminium oxyhydroxide (see Fig. 8).

Analogous results were found by Gomes et al. [20]. According to their research, Bragg reflections possessing very broad humps and low intensity indicate that the analyzed phase possesses a short-range order, i.e., amorphous or very poorly crystalline in nature. Because crystallization of aluminium hydroxides/oxyhydroxides is a very slow process, most aluminium hydroxides and oxyhydroxides found to be either amorphous or very poorly crystalline. Because of their short-range order, these hydroxides/oxyhydroxides gave broad and diffuse XRD peaks, making them very difficult to identify. The above authors also identified phases in EC aluminium product via XRD, and their most likely nature are aluminium hydroxide bayerite ( $\text{Al}(\text{OH})_3$ ) and aluminium oxyhydroxide diasporite ( $\text{AlO}(\text{OH})$ ).

Further, the XRD analysis shows several peaks which were identified to be cryolite  $\text{Na}_3(\text{AlF}_6)$  (blue line) and sodium aluminium fluoride  $\text{Na}_5\text{Al}_3\text{F}_{14}$  (red line).

### 3.4.2. Scanning electron microscope and energy dispersive X-ray analysis

To evaluate the structural features of the sludge generated by the electrochemical process, scanning electron microscopy

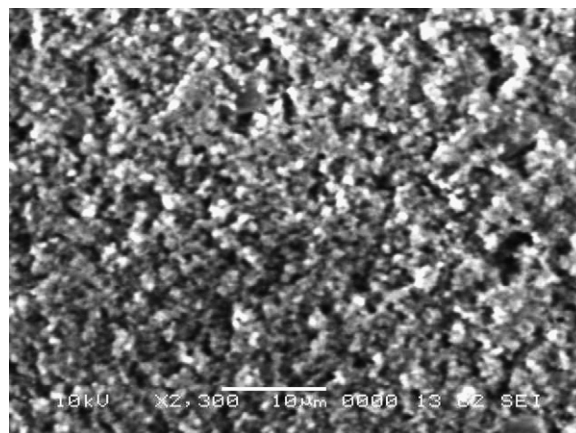


Fig. 6. SEM image of the sludge produced in the electrochemical process.

experiments were performed. As shown in Fig. 6, the SEM image indicates the presence on the surface of mostly amorphous or ultrafine particular structure at micrometer size.

Energy dispersive analysis of X-rays was used to analyse the elemental constituents of the defluoridation sludge. Fig. 7 confirmed the presence of removed fluoride  $\text{F}^-$  in the settled sludge. The other peaks indicate that oxygen, aluminium, and sodium are present in the sludge.

This information confirms that once the colloidal matter is destabilized, it can be separated from the wastewater and that the aluminium generated by the electrolysis forms complexes with the fluoride in the sludge. The detected elements in the product come from the adsorption of the conducting electrolyte.

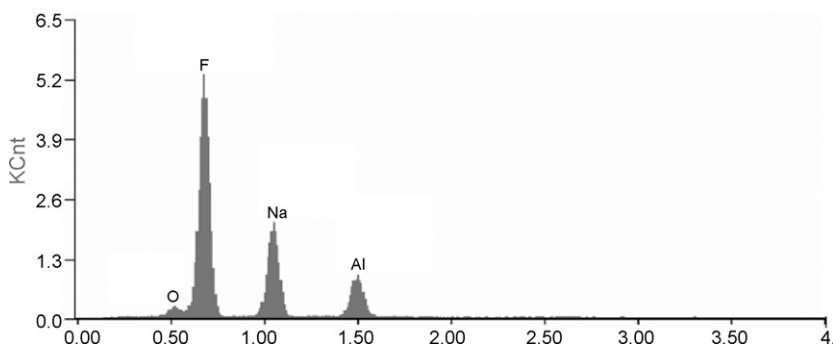


Fig. 7. Energy dispersion spectrum of the sludge produced in the electrochemical process.

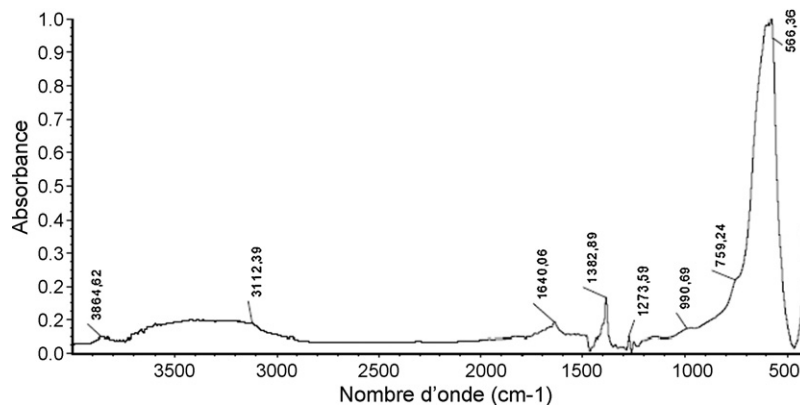


Fig. 8. FT-IR spectrum of the sludge produced in the electrochemical process.

### 3.4.3. Fourier transform infrared spectroscopy

According to Fig. 8, infrared analysis of aluminium electrode by-product showed two bands at 3864 and 3112  $\text{cm}^{-1}$  which correspond most likely to O–H stretching vibrations, that at 1640  $\text{cm}^{-1}$  to hydroxyl bending and  $\gamma'(\text{OH})$  water bending vibration or overtones of hydroxyl bending. Al–O–H bending is represented by the band at 990  $\text{cm}^{-1}$ , that at 1382  $\text{cm}^{-1}$  to Al–H stretching, and 1273  $\text{cm}^{-1}$  represents the characteristic stretching bands of Al=O. The band at 566  $\text{cm}^{-1}$  may be ascribed to the stretching of Al–OH.

## 4. Conclusion

The EC method was successfully used in treating solutions containing fluoride. This electrochemical technique has been applied to produce  $\text{Al}^{3+}$  with an aluminium anode.

The experimental results showed that the quality of EC treated solution depends on the amount of coagulant produced which is closely dependant on applied potential and electrolysis time.

The addition of supporting electrolyte has a positive effect on fluoride removal. It can also cause the raising of the electrical conductivity of the water leading to less passing current through the circuit.

XRD pattern shows several peaks which were attributed to aluminium fluoride complexes.

From XRD, and FT-IR analysis of the Al electrode sludge, it is concluded that the chemical speciation of the by-products can be mostly aluminium hydroxide and/or aluminium oxyhydroxides.

XRD spectrum and SEM photographs demonstrated amorphous phase and very fine structure for aluminium hydroxide/oxyhydroxides.

The existence of the fluoride on the produced sludge was proved experimentally with the help of EDAX, indicating that the aluminium generated by the electrolysis forms complexes with the fluoride ions.

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