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Fluoride Removal from pretreated Photovoltaic Wastewater by Electrocoagulation: An Investigation of The Effect of Operational Parameters

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Abstract

In this paper, application of electrocoagulation using common iron electrode to a simulated photovoltaic wastewater after precipitation with lime ($\text{Ca}(\text{OH})_2$) was investigated. Electrocoagulation process delivers the coagulant in situ as the sacrificial anode corrodes, while the simultaneous evolution of hydrogen at the cathode allows pollutant removal by flotation. Several working parameters, such as initial pH, applied potential and distance between the electrodes, were studied in an attempt to achieve higher fluoride removal efficiency. The optimum conditions for the process were identified as pH = 6, the distance between electrodes = 1 and an applied potential of 30 V. Furthermore fluoride removal is under the direct discharge standards. Results showed high effectiveness of the electrocoagulation method in removing fluoride from aqueous solutions.

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Keywords: Wastewater; Electrocoagulation; Fluoride; Iron electrode; Photovoltaic wastewater

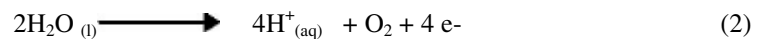
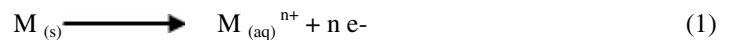
1. Introduction

Wastewater in photovoltaic industry can generally be divided into three streams, namely acid-base, chemical mechanical polishing and fluoride-containing. Fluoride-containing wastewater comes from an etching and rinsing operation. Several methods have been investigated on the treatment. An electrocoagulation process using aluminum electrodes can treat fluoride-containing wastewater [1-3], adsorption and biosorption [4-6], adsorption on natural materials [7], ion-exchange [8], chemical precipitation including electrocoagulation/flotation [9,10], and membrane

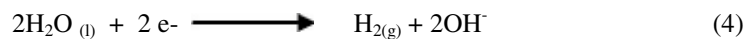
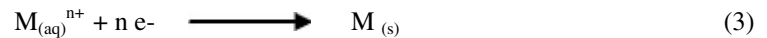
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processes, such as reverse osmosis [11], Donnan dialysis [12], nanofiltration [13], and electro dialysis [14]. Photovoltaic wastewater containing fluoride is treated in a common conventional treatment system consisting of calcium fluoride precipitation, flocculation and solid/liquid separation. Fluoride removal by precipitation as calcium fluoride is one of the most established and well defined processes to remove high concentration of fluoride from a photovoltaic wastewater. Calcium salts such as calcium chloride and calcium hydroxide may be used to precipitate fluoride as insoluble calcium fluoride salt [15]. Electrocoagulation can be used to achieve standard limits discharge that cannot be achieved by precipitation [16]. The suitable level of fluoride in drinking water specified by the World Health Organization (WHO) is 1.5 mg L^{-1} [17]. The discharge standard of fluoride in industrial wastewater is 15 mg L^{-1} in Algeria [18]. EC is a process consisting of creating metallic hydroxides flocks within the wastewater by electro-dissolution of soluble anodes, usually made of iron or aluminum. Fe/Al is dissolved from the anode generating corresponding metal ions, which immediately hydrolyze to polymeric iron or aluminum hydroxide. These polymeric hydroxides, and their subsequent precipitation, are similar to the processes that occur during coagulation (or flocculation) and precipitation using alum or other chemical coagulants [17]. A simple electrocoagulation reactor is made up of one anode and one cathode. When a potential is applied from an external power source, the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals [19]. The electrochemical reactions with metal M as anode may be summarized as follows:

At the anode:



At the cathode:



In water and wastewater treatment, electrocoagulation has been widely used to treat potable water, urban wastewater, oil wastes, textile wastewater [20], suspended particles, chemical and mechanical polishing waste [21], fluoride-containing water [22], and heavy metal containing solutions [23-32]. Compared with traditional flocculation-coagulation, electrocoagulation has also, in theory, the advantage of removing the smallest colloidal particles; such charged particles have a greater probability of being coagulated and destabilized because of the electric field that sets them in motion [33]. Electrocoagulation has the advantage of producing a relatively low amount of residue also [34-36].

2. Material and Methods

2.1. Experimental apparatus and procedure

Fig. 1 shows the experimental setup. It consists of a parallelepiped reactor made of plexiglass with 1L capacity and its base consists of two inclined plates to promote the settling of sludge formed. The dimensions of the reactor were (114mm×140mm). The EC experiment was operated in batch mode with recirculation of the liquid in the circuit which consists of a Fontaine M7 pump. The iron 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^2 . The DC power supply was a P. Fontaine MC 3030C generator. Cell potential was controlled by a voltmeter. Wastewater samples were taken every 10 min for water quality measurements. A selective ion sensor electrode [PF4L from Tacussel (Lyon)] [37] was used to determine the F^- concentration according to the standard method given by the American Public Health Association [37,38].

To prevent the interference from other ions (Al^{3+} , Fe^{3+} , Cu^{2+} , Ca^{2+} , ...), TISAB II buffer solution containing CDTA (cyclohexylenediaminetetraacetic acid, Orion Research Inc.) was added to the samples.

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 pretreated photovoltaic wastewater.

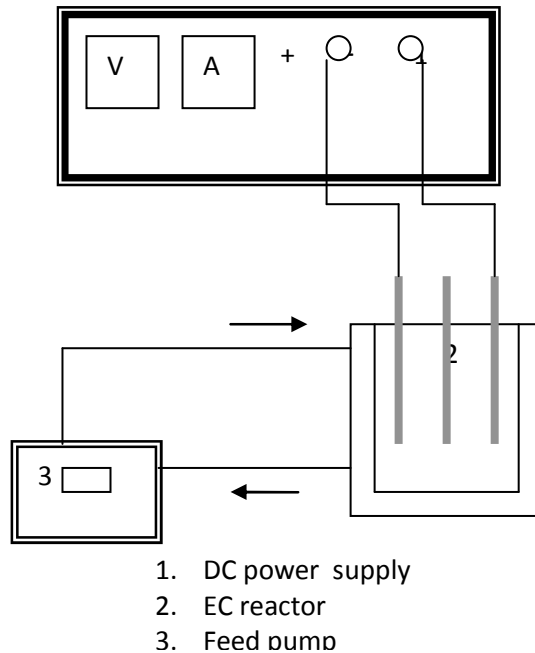


Fig.1. Schematic diagram of the defluoridation experimental setup.

3. Results and discussion

3.1. Effect of applied potential

Applied potential is very important in electrocoagulation because it is the only operational parameter that can be controlled directly. In this system, electrode spacing is fixed and current is a continuous supply. Applied potential directly determines both coagulant dosage and bubble generation rates and strongly influences both solution mixing and mass transfer at the electrodes.

To investigate the effect of applied potential on the fluoride removal, a series of experiments were carried out under the experimental conditions of applied potential being varied from 10 to 30 V for iron electrodes. Fig. 2 illustrates that the fluoride removal increased quickly by increasing the applied potential. As the applied potential was increased from 10 to 30 V, the time needed to achieve standard limits discharge of fluoride for iron electrode decreased. The fluoride removal rise significantly and reaches standard limits in 40 minutes for applied voltage of 30V, whereas for 20 and 10V more time is needed to achieve the same results. This is mainly due to insufficient amount of electric power at lower voltages to produce iron coagulant species and gas bubbles responsible for defluoridation. According to Faraday's law, increasing the applied potential leads to a higher coagulant dosage per time unit.

$$m = \frac{Mit}{nF} \quad (5)$$

Where m is the quantity of electrode material dissolved (g), i is the current density (A), t is the time in s; M is the relative molar mass of the concerned metal, n is the number of electrons in oxidation reaction, and F is the Faraday's constant, $96,500 \text{Cmol}^{-1}$.

These results were reported by several authors, Mameri et al. [39] reported that during wastewater containing fluoride treatment with iron electrodes, higher applied potential allows increasing the amount of iron dissolved or deposited to the bulk solution and can be achieved by leading adsorption and increasing the removal efficiencies of fluoride ions.

Chen-Lee Lai et al.[40] have confirmed that increasing the applied potential leads to higher dissolution of iron electrode allowing increasing of metal species required to remove contaminants.

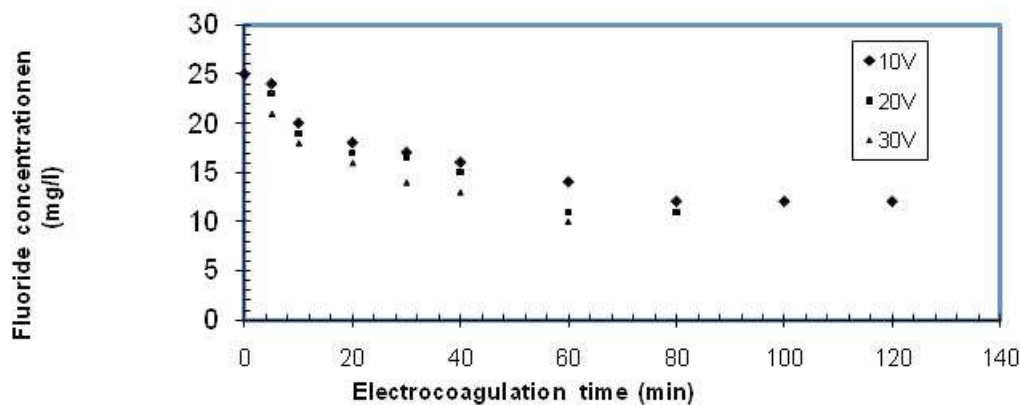


Fig. 2. Influence of the fluoride concentration on the electrocoagulation process, $T = 20^\circ\text{C}$, $I = 1\text{A}$, treated volume 1 L.

3.2. Effect of pH

pH of the solution plays an important role in electrochemical and chemical coagulation process [41]. Under certain conditions, various complex and polymer compounds can be formed via hydrolysis and polymerization reaction of electrochemically dissolved iron ions.

Hence experiments were conducted to study the effect of pH on the fluoride removal. The effect of pH on the fluoride removal was examined in the range of 4 to 9. Applied potential of 30 V was kept constant in the experiments. The results obtained are shown graphically in Fig. 3 for 25 mg/L fluoride concentration.

The results revealed that when pH of the treated solution was between 6 and 7, there was maximum fluoride removal because the initial pH value of the treated solution was around 6. Hence, there is no need for the addition of chemicals to change the initial pH values.

Under these conditions synthetic fluorinated solution water reached the concentration recommended by the standards discharge after 40 min for pH 6. Therefore, it can be concluded that at this range of pH, the majority of iron complexes (coagulants) are formed and it is the optimum pH for carrying out the electrocoagulation. From the Pourbaix diagram [42], it can be deduced that the major coagulant species formed at this pH are $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$. This may be illustrated with an iron from Pourbaix's diagram presented in Fig. 4.

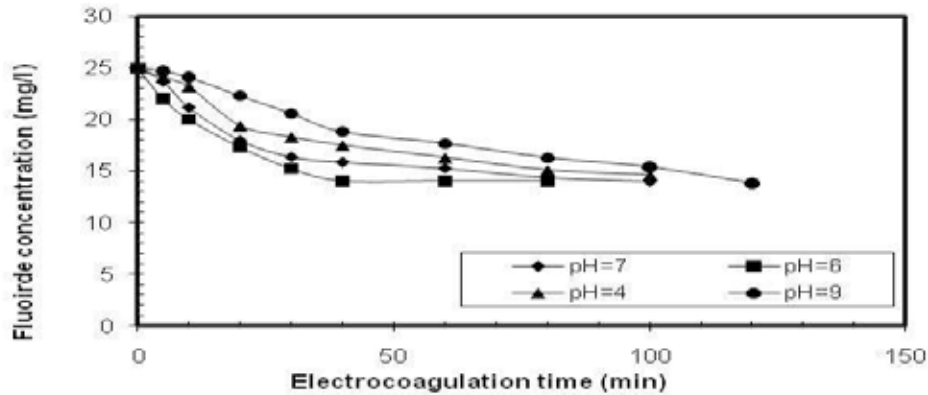


Fig. 3 .Influence of PH on fluoride removal, $T = 20^{\circ}\text{C}$, $I = 1\text{A}$, treated volume 1 L.

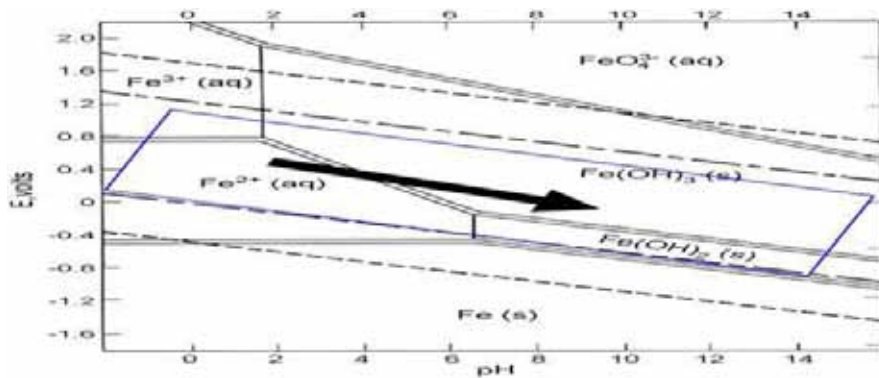


Fig. 4. Iron Pourbaix diagram, showing the region and direction in which the EC process proceeds [42].

3.3. Effect of distance between electrodes

In electrocoagulation, when the distance of the electrodes increases, the electrical current is decreased since the ohmic potential drop is proportional to the inter-electrode distance. Reducing this distance is of great importance for reducing the electrolysis energy consumption especially when the conductivity is low. For this reason, investigation of this parameter is helpful. When the distance of the electrodes increased from 1 to 2 cm, the time needed to achieve standards limits of fluoride is decreased from 100 to 40 min with applied potential of 30 V. These results are shown in Fig.5. The results reveal improved fluoride removal at smaller inter-electrode distance.

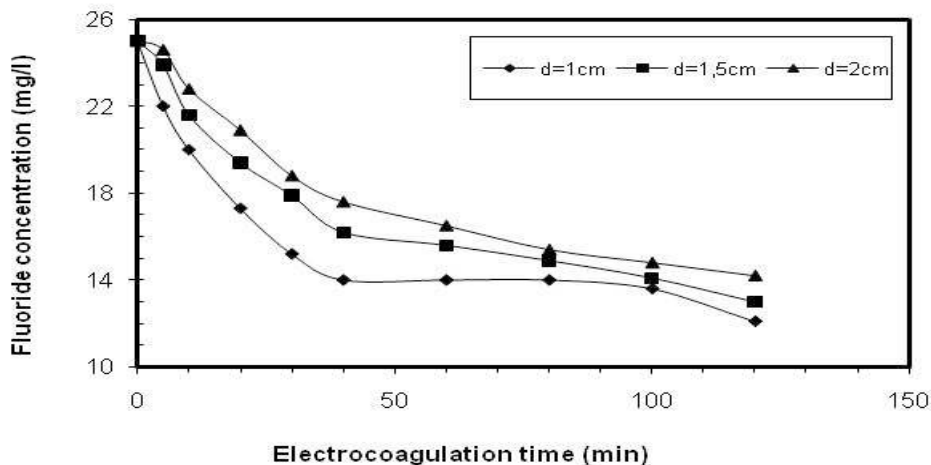


Fig. 5. Influence of the distance between electrodes on fluoride removal, $T = 20^{\circ}\text{C}$, $I = 1\text{A}$, treated volume 1 L.

4. Conclusion

Results of this study on fluoride removal from pretreated photovoltaic wastewater with electrocoagulation can be summarized as follows:

- The electrocoagulation process is successfully applied to remove fluoride from pretreated photovoltaic aqueous solution. The Defluoridation was found to be dependent on the initial pH distance between electrodes and the applied potential.
- The most effective conditions to achieve standard discharge for fluoride by electrocoagulation was obtained with typical operating conditions; 30 V applied potential, 40 min operating time and pH 6.
- Preliminary assessment of the process was carried out, and some implications for operation and process modification.
- Future work should include the influence of residence time, energy consumption, initial concentration of fluoride and the presence of other elements in pretreated wastewater in order to scale-up the process.

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