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Fluoride removal from photovoltaic wastewater by aluminium electrocoagulation and characteristics of products

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In this work, treatment of synthetic fluoride-containing solutions by electrocoagulation (EC) method using aluminium electrodes has been studied in order to treat wastewater from photovoltaic wafers production industry. EC was investigated for applied potential (10-30V), electrolysis time and supporting electrolyte (NaCl) concentration (0–100 mg/L). Our results showed that with increasing applied potential and electrolysis time, the Al^{+3} dosage increases too, 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.

Keywords: sludge structure, fluoride, electrocoagulation fluoride removal.

1. Introduction

Fluoride ion in water has been found to have a significant effect against dental caries WHO (2004). Fluoride ion in water has both beneficial and harmful effects on the environment and the human. In PV manufacturing hydrofluoric acid (HF) is used extensively for wafer etching and quartz cleaning operations Huang et Liu (1999). There are several defluoridation processes that have been tested globally, such as adsorption Lounici et al (1999), chemical precipitation Sujana et Thakur (1998), electrodialysis Amor et al (2001), and electrochemical method Ming et al (1983), Drouiche et al (2007). In Silicon Technology Development Unit a conventional treatment described above is used to process the polluted acids and alkaline waste Li et Kiang (2003). The physico-chemical treatment consists firstly on lime addition because high fluoride concentration is present, this stage can reduce the residual fluoride concentration to 15–20 mg/L, Saha (1993). This step is followed by coagulation/flocculation. Flocculation is always used in conjunction with and preceded

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by coagulation. The process of coagulation allows particle agglomeration and enhances subsequent particle, this process is complex and may be involve several mechanisms to achieve destabilization of negatively charged particles, it result a repulsive force that tend to stabilize the suspension matter and prevent particle agglomeration Semerjian et Ayoub (2003). Flocculation is the physical process of bringing the destabilized particles in contact to form larger flocks that can be easily removed from suspension. At Last the treated wastewater strained through a filtration system in order to separate aqueous phase from solids matters Mesdaghinia et al (2005).

The objective of this work was to investigate the treating of PV wastewater by electrocoagulation. The major objectives of this study are to determine the influence on defluoridation process of the operating variables such as applied potential, electrolysis time and supporting of electrolyte. The morphology and characterization of the sludge was characterized using FTIR, DRX, scanning electron microscopy (SEM) and energy dispersion spectra (EDS).

2. Materials and methods

2.1. Chemicals

In order to simulate the photovoltaic wastewater, after calcium precipitation, desired concentrations of F^- solution were prepared by mixing proper amount of sodium fluoride procured from Prolabo, Paris, France with D.I. water.

2.2. Chemical analysis

The concentration of fluoride was measured using an ion meter Jenway 3205 equipped with Jenway fluoride combination ion selective electrode. Total ionic strength adjustment buffer (TISAB) at pH 5.4 was used to maintain constant ionic strength and to prevent the interference from other ions such as Al^{3+} and Ca^{2+}.

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

The PXRD analysis of the electrocoagulation by-products were carried out with a Bruker AXS D4 Endeavor diffractometer operating with a Cu K_α radiation source and filtered with a graphic monochromator (λ = 1.5406 °A).

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

2.3. Experimental procedures of electrocoagulation

The experimental setup is schematically shown in Fig.1. The defluoridation apparatus consisted of an EC reactor with effective volume of 1 L. The EC chamber had three aluminum electrodes, each with an effective area of 170 cm^2. The aluminum electrodes were connected in a bipolar mode. The current input of the DC power supply was maintained constant, by means of a precision DC power supply (P.Fontaine MC 3030C). The DC power supply was turned on with a voltage kept at a desired value of 10, 20 and 30 V. Well mixing of the synthetic solution during electrocoagulation process was provided by means of the centrifugal Fontaine M7 feed pump, which allows flow rates of up to 460 L/h . The purity of the aluminium electrodes used was about 99.8%. Electrodes were sanded and washed with dilute HCl before each experiment. Experiments were conducted with temperature of around 25°C.

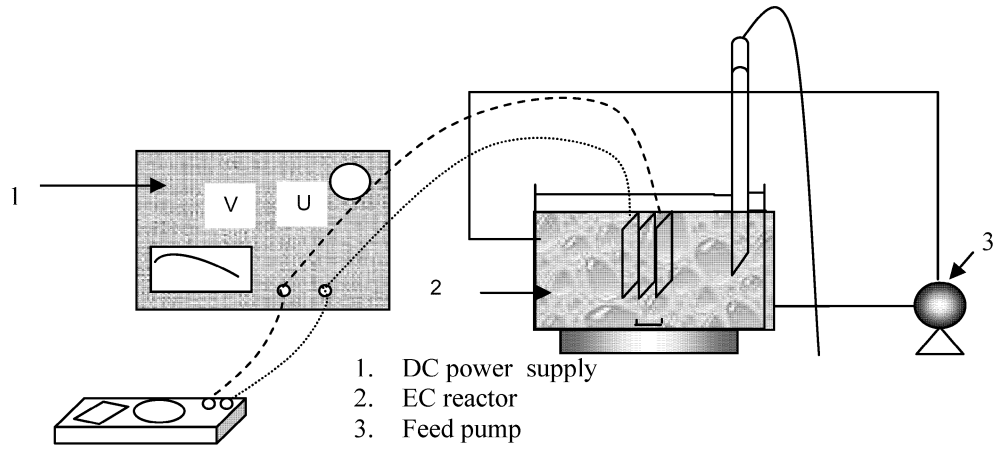


Fig.1. Schematic electrocoagulation reactor

3. Results and discussion

3.1. Effect of applied potential and electrolysis time

The applied potential and electrocoagulation time determines the coagulant dosage rate. Thus, this parameter should have a significant impact on removal efficiency of fluoride. To investigate the effect of applied potential and electrolysis time on the fluoride removal, a series of experiments were carried out by solutions containing a constant fluoride concentration of 20 mg/l loading with applied potential being varied from 10 to 30 V. The 6.0 of solution of pH and flow rates of up to 460 L h^{-1} allowing well mixing were kept constant in experiments. Consequently, fluoride removal increased with increasing applied potential because more Al^{3+} passed to solution and consequently formation rate of $Al(OH)_3$ increased. As a result of increasing applied potential, current density increased. The results obtained were shown graphically in Fig.2, it reveals that the maximum concentration limit as per Algerian standard discharge for F^-(15 mg/l) is obtained after 60 min of EC with applied potential of 30 V. For applied potential of 10 and 20 V the standard discharge limit of fluoride was obtained in more time.

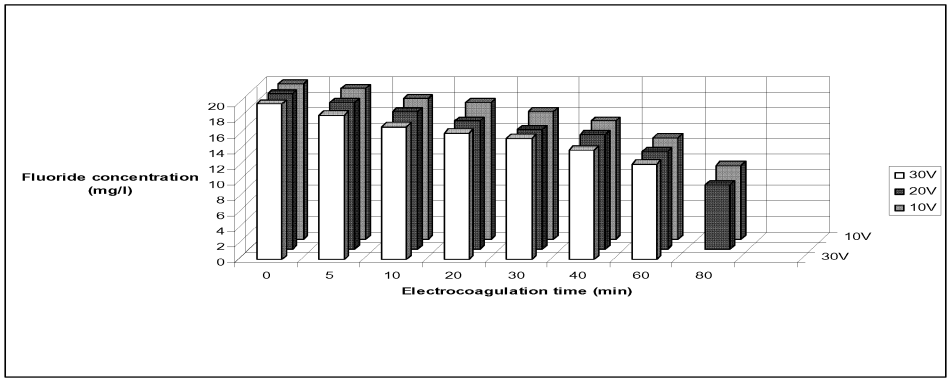


Fig.2 Fluoride residual concentration as a function of electrolysis time and applied potential.

3.2. Effect of supporting electrolyte

The effect of supporting electrolyte on the fluoride removal was examined with NaCl, applied potential of 30 V, flow rates of up to 460 L h^{-1} and pH of 6 were kept constant in the experiments. Supporting electrolyte was examined for fluoride concentration of 20 mg/L. Removal increased with increasing of supporting electrolyte, the highest fluoride removal was observed with 100 mg/l. The results obtained were shown graphically in Fig.3 In addition, the energy consumption decreased with increasing concentration of supporting electrolyte because current density decreased under constant applied potential.

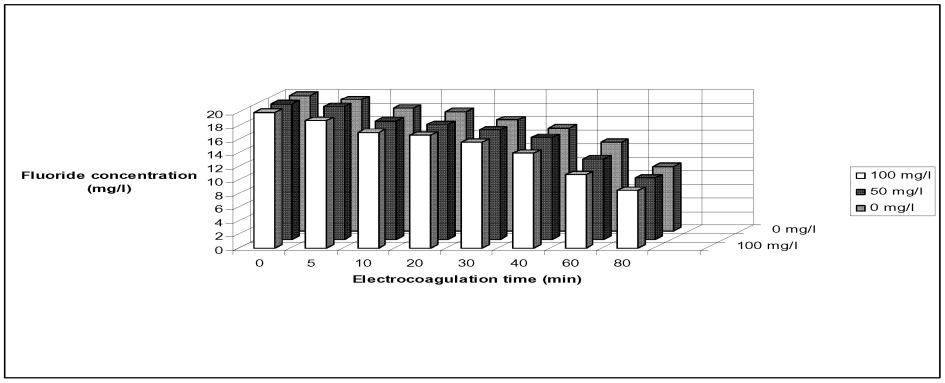
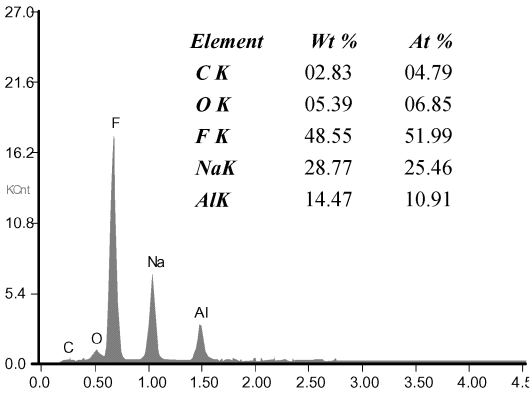


Fig.3 Fluoride residual concentration as a function of supporting electrolyte.

4. Characteristics of sludge

4.1. SEM/EDAX

Based on the SEM/EDS result (see Fig.4), fluoride, sodium and aluminium were determined to be the main component of the sludge in the wastewater resulting from electrocoagulation. The SEM image indicates the presence of mostly amorphous or ultrafine particular structure at μm size on the surface. The elemental analysis by EDAX confirmed the presence of F removed (51.99 at. %) from the sample solution. Others elements detected in the sludge come from the adsorption of the conducting electrolytes, chemicals used in the experiments and the scrap impurities of the Al electrodes.



Element	*Wt %*	*At %*
C K	02.83	04.79
O K	05.39	06.85
F K	48.55	51.99
NaK	28.77	25.46
AlK	14.47	10.91

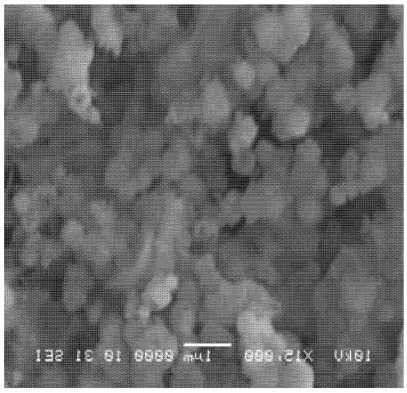


Fig.4. The ESEM/EDS pattern of dried sludge.

4.2. Fourier transform infrared spectroscopy (FTIR)

The electro co-precipitated sludge generated during electrocoagulation was analyzed using FT-IR spectrometer. A 10–15 mg of sample was dispersed in 200 mg of spectroscopic grade KBr to record the spectra. Scans were collected at a resolution of 4 cm^{-1}. The wave numbers ranged from 4000 to 500 cm^{-1}. The result was shown in Fig.5 Peaks at 3860 and 3420 cm^{-1}corresponding to H–O–H bond stretching at 1640 cm^{-1} to hydroxyl bending and γ′(OH) water bending vibration or overtones of hydroxyl bending**.** Peaks at 1270 605 cm^{-1} are corresponding to Al–O and Al–F–Al bond stretching respectively. Al–F–Al bond stretching was matched with the analysis made by Gross et al (2007) for various amorphous tri- fluoride complexes. From this analysis, it was confirmed that fluoride was linked with aluminium hydroxide complexes and precipitated at the bottom of EC Ghosh et al (2008).

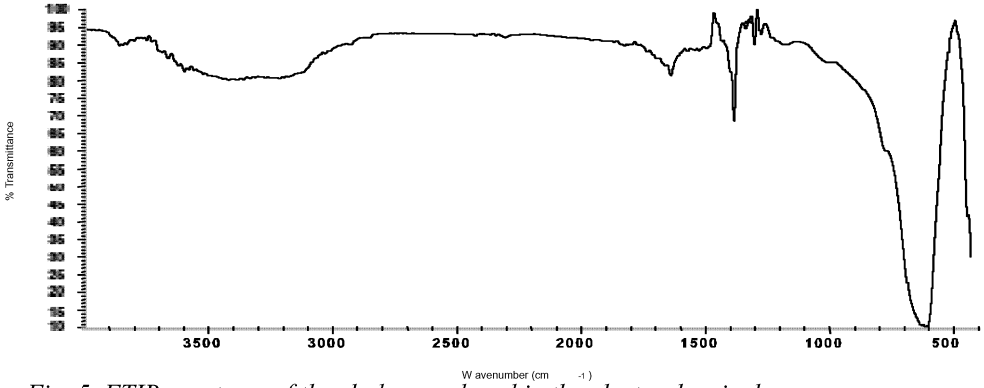


Fig. 5. FTIR spectrum of the sludge produced in the electrochemical process.

4.3. X-ray analysis

To confirm the mechanism of fluoride removal, the composition of the sludge produced by electrocoagulation was analyzed using X-ray diffraction (XRD) spectrum at the final pH of 6. It is believed that precipitation or adsorption reaction may occur when aluminium electrodes is used for fluoride removal Shen et al (2003). As seen in Fig. 6, the strongest peaks appeared were identified to be cryolite ($Na_3(AlF_6)$ and sodium aluminium fluorite ($Na_5Al_3F_{14}$). At pH 6 amorphous $Al(OH)_3$ formed adsorb F^- and this is beneficial for a rapid adsorption of soluble compounds and colloids particles. This is the main reason for defluoridation by electrocoagulation process.

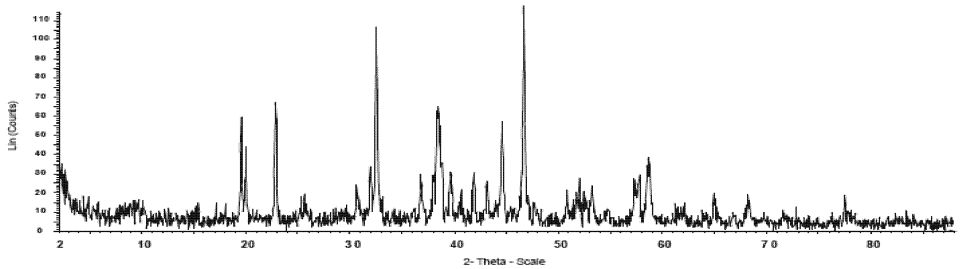


Fig.6. XRD diagram for aluminium sludge produced in the electrochemical process.

5. Conclusion

Batch flow experiments were designed to investigate the effects of the different parameters including applied potential, electrolysis time and supporting electrolyte on the fluoride removal efficiency by EC process. The residual fluoride concentration reaches from 20 to 13 mg/L when applied potential was 30V and electrolysis time of 60 min and it's was below the discharge standards in Algeria. Slight rising in removal efficiency is observed with increased addition of NaCl as supportive electrolyte.

XRD analysis of the composition of the dried sludge obtained by EC process shows the formation of be cryolite ($Na_3(AlF_6)$ and sodium aluminium fluorite ($Na_5Al_3F_{14}$) and this is the main reason for defluoridation by electrocoagulation process.

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