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HF wastewater remediation by electrocoagulation process

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ABSTRACT

Wastewater from surface treatment of silicon wafers is rich in fluoride ions. This is attributed to the use of hydrofluoric acid in huge quantities during stripping operation. Lime precipitation is insufficient to comply with environmental standards. In this work, the electrocoagulation (EC) was used for polishing treatment after neutralizing step. Synthetic solutions were used for the investigation into main operational factors affecting fluoride removal performance such as electrode material, initial pH, current density, salt nature, etc. The experimental results showed that EC is efficient for the removal of fluoride ions. This performance is ascribed to the effect of anodically generated coagulants. A removal efficiency of more than 99% of fluoride may be obtained. The quality of the effluent water met the specifications for the national discharge standard.

Keywords: Photovoltaic cell; HF wastewater; Fluoride removal; Electrocoagulation

1. Introduction

The photovoltaic cell industry is growing very fast in the past few years. The manufacturing of cells requires large volumes of ultra-pure water and considerable amounts of chemicals and therefore generates large volumes of wastewaters. During manufacturing, huge quantities of hydrofluoric acid (HF) are used in etching and cleaning of silicon wafers. Hence, effluents from this process contain high levels of fluoride. Typical fluoride concentrations are from 1,000 to 3,500 mg/L [1,2]. The discharge of such wastewater into the surface water would lead to the contamination of groundwater. Long-term drinking of water that containing high fluoride content can result in mottling of teeth, softening of bones, ossification of tendons and ligaments and several neurological damages in severe cases [1,3].

Due to its high toxicity, industrial wastewater containing fluoride is strictly regulated. Environmental authorities limit fluoride discharge levels to 15 mg/L or less.

The most commonly used way to remove fluoride ions from wastewater is to form calcium fluoride (CaF_2) by adding excess of lime according to the following reaction:

$$Ca(OH)_2 + 2HF \leftrightarrow CaF_2 + 2H_2O \qquad (1)$$

In spite of its advantages, lime precipitation is insufficient to comply with environmental standards. In practice, the precipitation can only reduce the fluoride concentration to 20–100 mg/L. Consequently,

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another defluoridation process must be performed. This is often carried out by chemical coagulation. Although it is simple and effective, it induces a secondary pollution by increasing the hardness of water and generating large volumes of sludge.

Electrocoagulation (EC) is an alternative technology for water and wastewater treatment systems. Compared with conventional chemical coagulation, it proved to be more effective in removing inorganic contaminants. EC is a potentially effective method for treating different kinds of wastewater with high removal efficiency [4]. EC process provides a simple, reliable and cost-effective method for the treatment of wastewater without any need for additional chemicals. It also reduces the amount of sludge which needs to be disposed. EC technique uses a direct current source between metal electrodes immersed in polluted water [5]. The electrical current causes the dissolution of metal plates into wastewater.

The metal ions, at an appropriate pH, can form wide ranges of coagulated species and metal hydroxides that precipitate and adsorb dissolved contaminants or destabilize and aggregate the suspended particles [4].

The most widely used electrode materials in EC process are aluminum and iron. In the case of aluminum, main reactions are given as follows:

$$\text{Anode}: \ \mathrm{Al_{(s)}} \rightarrow \mathrm{Al^{3+}} + 3\mathrm{e^{-}} \tag{2}$$

$$\text{Cathode}: 3\mathrm{H_2O} + 3\mathrm{e^{-}} \rightarrow (3/2)\mathrm{H_{2(g)}} + 3\mathrm{OH^{-}} \tag{3}$$

$$\mathrm{Al^{3+}} + 3\mathrm{H_2O} \rightarrow \mathrm{Al(OH)_3} + 3\mathrm{H^{+}} \tag{4}$$

Freshly formed amorphous $Al(OH)_{3(s)}$ flocs have large surface areas, which are beneficial for a rapid adsorption of soluble compounds and trapping of colloidal particles. Finally, these flocs are removed easily from aqueous medium by sedimentation or flotation.

The EC process has successfully been used for the treatment of wastewaters including electroplating wastewater [6], laundry wastewater [7] and photovoltaic wastewater [7]. Meanwhile, EC process has been widely used to decolorize various textile wastewaters [8,9].

The aim of this study is to conduct an experimental investigation into the removal of fluoride ions, using the EC method. The effects of operational parameters such as electrolysis time, electrode material, initial pH, current density and salt nature on fluoride removal efficiency have been investigated in this laboratory scale study.

2. Experimental

2.1. Materials and methods

2.1.1. Chemicals

The stock solutions used in this study were prepared with reagent-grade chemicals and reverse osmosis (RO)-deionized water. Standard acid and base solutions (0.1 N HCl and 0.1 N NaOH solutions) were prepared for pH adjustment.

Fluoride stock solution was prepared by dissolving 2.21 g of anhydrous sodium fluoride (99.0% NaF, MERK) in 1,000 mL deionized water in volumetric flask. Standard solutions at a required concentration range were prepared by appropriate dilution of the stock solution.

2.1.2. Experimental setup

The batch experimental device is schematically shown in Fig. 1. The EC unit consists of an electrochemical reactor which is a glass beaker with magnetic stirring, a DC power supply (ELEKTROLYSER, ELYN1 brand.) and two electrodes.

The cathode and anode consist of separated sheets, each one with dimensions of (5 cm × 15 cm × 0.2 cm.) The submerged surface area of the each electrode plate was 50 cm^2. They were placed vertically and dipped in 1,000 mL aqueous fluoride solutions. The gap between the electrodes was 1.5 cm except indication.

An ammeter (PHYWE) and voltmeter (DIGITAL VOLTMETER (G-1002-500)) were used to check the current and the voltage during EC process.

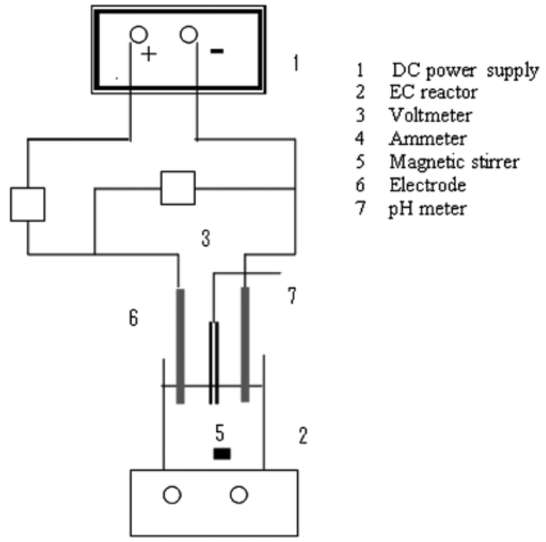

Fig. 1. Diagram of the experimental setup for the EC process.

2.1.3. Procedure

All the runs were performed at room temperature. A gentle magnetic stirring rate of about was applied to the solutions in all tests. The total time duration of electrolysis was 90 min for most test runs unless noted otherwise. Solution pH is monitored. Samples were periodically withdrawn and filtered through a 0.2-μm filter in order to measure the fluoride concentration.

2.2. Chemical analysis

A selective ion sensor electrode (PF4L from Tacussel (Lyon)) was used to determine the fluoride concentration, according to the standard method given by American Public Health Association [10]. To prevent the interference from other ions (Al^{3+}, Fe^{3+}, Cu^{2+}, Ca^{2+} …), the total ionic strength adjustment buffer (TISAB II) solution containing CDTA (Cyclohexylenediamine-tetraacetic acid, Orion Research Inc.) was added to samples.

The pH values were determined by using Sension1 pH meter (HACH), while conductivity was measured by a conductivity meter model 4071 (JENWAY).

Fourier transform infrared spectroscopy (FTIR) was performed using potassium bromide pellets. Infrared analysis was carried out with Perkin-Elmer paragon 1000 spectrum RX, and the results were obtained with OMNIC™ software.

The calculation of fluoride removal efficiency *R* (%) by EC treatment was performed using this formula:

$$R(\%) = \frac{(C_0 - C)}{C_0}100 \tag{5}$$

C_0: Initial fluoride concentration.
C: Fluoride concentration at time t.

3. Results and discussion

3.1. Effect of electrode pair nature

Three experiment sets were carried out by varying the nature of the anode–cathode material: Aluminum–Aluminum (Al–Al), Iron–Iron (Fe–Fe) and Aluminum–Stainless Steel (Al–SS). These pairs were chosen because they are often encountered in EC applications. The best results were obtained with the pair (Al–Al) with 62% against 16.8% for (Fe–Fe) pair. This is likely due to the higher affinity of aluminum coagulants comparing with iron ones toward fluoride. The superiority of the pair (Al–Al) on (Al–SS) one is may be due to the additional coagulant production by chemical attack on the aluminum cathode. This was confirmed by the cathode weight loss observed during EC process. Bensadok et al. [11] found that higher removal efficiencies were obtained with (Al–Al) compared to (Al–Ti/Pt). This was explained by the additional dissolution of Al cathode, which contributes to

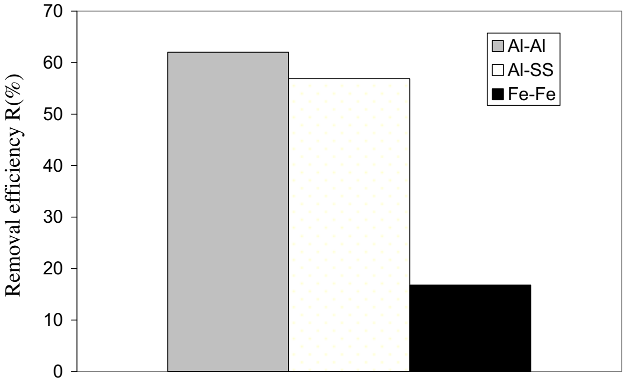

Fig. 2. Effect of electrode pair nature on fluoride removal efficiency. $pH_0 = 7$; $i = 2\,mA/cm^2$, [NaCl]=0.01 M; $[F]_0 = 50\,mg/L$, $t = 90$ min.

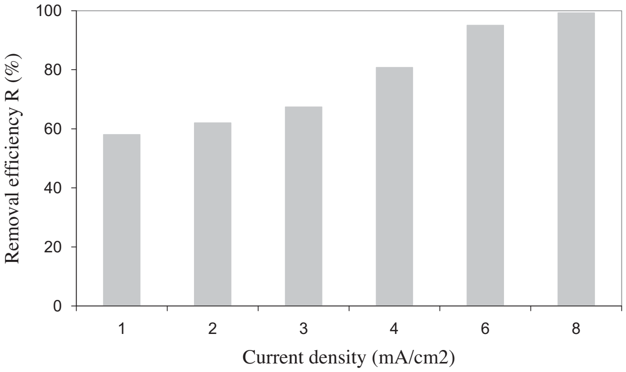

Fig. 3. Effect of current density on the removal efficiency. $pH_0 = 7$; [NaCl]=0.01 M; $d = 1.5$ cm; initial concentration, 50 mg/L; electrolysis time, 90 min.

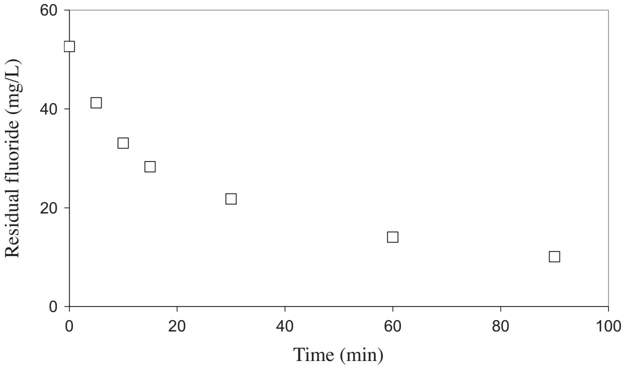

Fig. 4. Effect of electrolysis time on the residual fluoride. $pH_0 = 7$; $i = 4\,mA/cm^2$, [NaCl]=0.01 M, $[F]_0 = 50\,mg/L$.

the pollutant elimination simply by higher amounts of Al (III) produced (see Fig. 2).

Such dissolution is caused by a chemical reaction involving hydroxide ions produced by water reduction (Eq. (3)) [12]:

$$2\mathrm{Al} + 6\mathrm{H_2O} + 2\mathrm{OH^-} \rightarrow 2\mathrm{Al(OH)_4^-} + 3\mathrm{H_{2(g)}} \tag{6}$$

3.2. *Effect of current density on fluoride removal efficiency*

Current densities ranging from 1 to 8 mA/cm^2 were used. Increasing current density results in improvement of fluoride removal efficiency by EC. This may explained by the production of more coagulating species generated by electrodissolution. Elimination efficiency of 95% was obtained with 6 mA/cm^2, while 8 mA/cm^2 gives more than 99% (see Fig. 3).

3.3. *Effect of electrolysis time*

Increasing treatment time improves fluoride removal. After 60 min of EC treatment, fluoride concentration dropped from de 50 to 14.05 mg/L (less than standard limit). Final concentration of 10.09 mg/L may be reached after 90 min of electrolysis time (see Fig. 4).

3.4. *Effect of initial pH*

In many processes of wastewater treatment, initial pH is the key parameter [13]. For that purpose, initial pH values ranging from 5 to 11 have been studied in order to examine its effect in fluoride removal. Results shown in Fig. 5 indicate that optimal pH is obtained between pH 5 and pH 7; the corresponding fluoride values are 8.75 and 8.61 mg/L, respectively. This result is in agreement with data from the literature. Mameri et al. [14] had found that EC optimum initial pH was around 5. Zuo et al. [15] found that optimal influent pH range is 6.0–7.0 at which effective EC defluoridation can be achieved. Furthermore, higher residual values are observed in the basic media (pH 9 and pH 11) with final fluoride of about 15.5 mg/L. The precipitate Al(OH)$_3$ is most prevalent between pH 6 and pH 8, and above pH 9, the soluble species $\mathrm{Al(OH)_4^-}$ is the predominant species [9].

3.5. *Effect of initial concentration*

In practice, after lime neutralization, different levels of fluoride concentration are recorded. Hence, many concentrations have been studied, from 12.5 to 100 mg/L. It can be seen that the weaker is initial concentration the weaker is residual fluoride. So, with 100 mg/L, residual fluoride is 40.7 mg/L, while with 12.5 mg/L, residual fluoride is 2.25 mg/L (see Fig. 7).

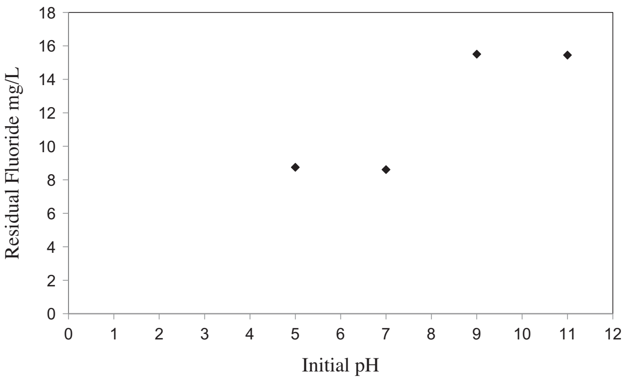

Fig. 5. Effect of initial pH on fluoride removal; $i = 4$ mA/cm^2, [NaCl] = 0.01 M, $t = 90$ min, $[\mathrm{F}]_0 = 50$ mg/L.

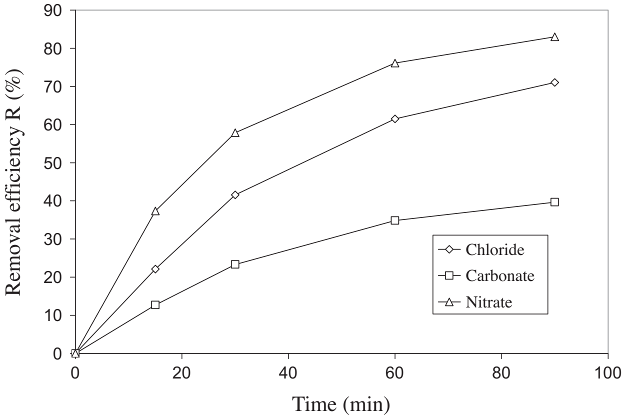

Fig. 6. Effect of anion nature on fluoride removal. $\mathrm{pH}_0 = 7$; $i = 4$ mA/cm^2, [anion] = 0.01 M, $t = 90$ min.

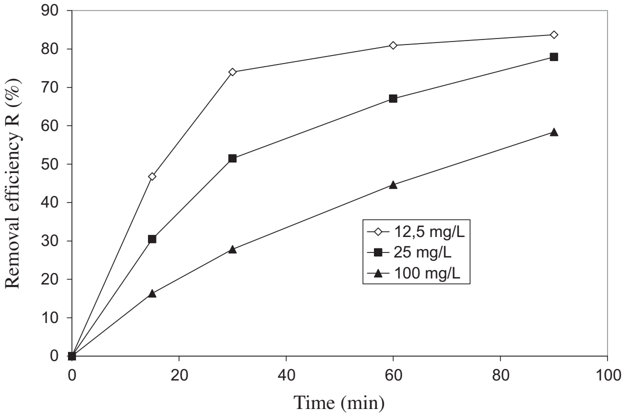

Fig. 7. Removal efficiency vs. initial concentration. $\mathrm{pH}_0 = 7$; $i = 4$ mA/cm^2, [NaCl]=0.01 M, $t = 90$ min.

3.6. Effect of salt nature

Effluents from photovoltaic industry contain most often huge quantities of anions such as chloride, carbonate, nitrate etc. These anions come from different salts and acids used together with HF in wafers cleaning operations. Consequently, the study of the effect of anions nature has been done. Three salts were chosen: NaCl, $NaNO_3$ and Na_2CO_3. Results show that the highest removal efficiencies were achieved with nitrate anions, while carbonate gives the lowest removal efficiencies (see Fig. 6).

3.7. Characterization of the by-products obtained from the EC by (FTIR)

EC by-product FTIR analyses were carried out in absence and presence of fluoride, in order to understand changes due to the presence of fluoride. From

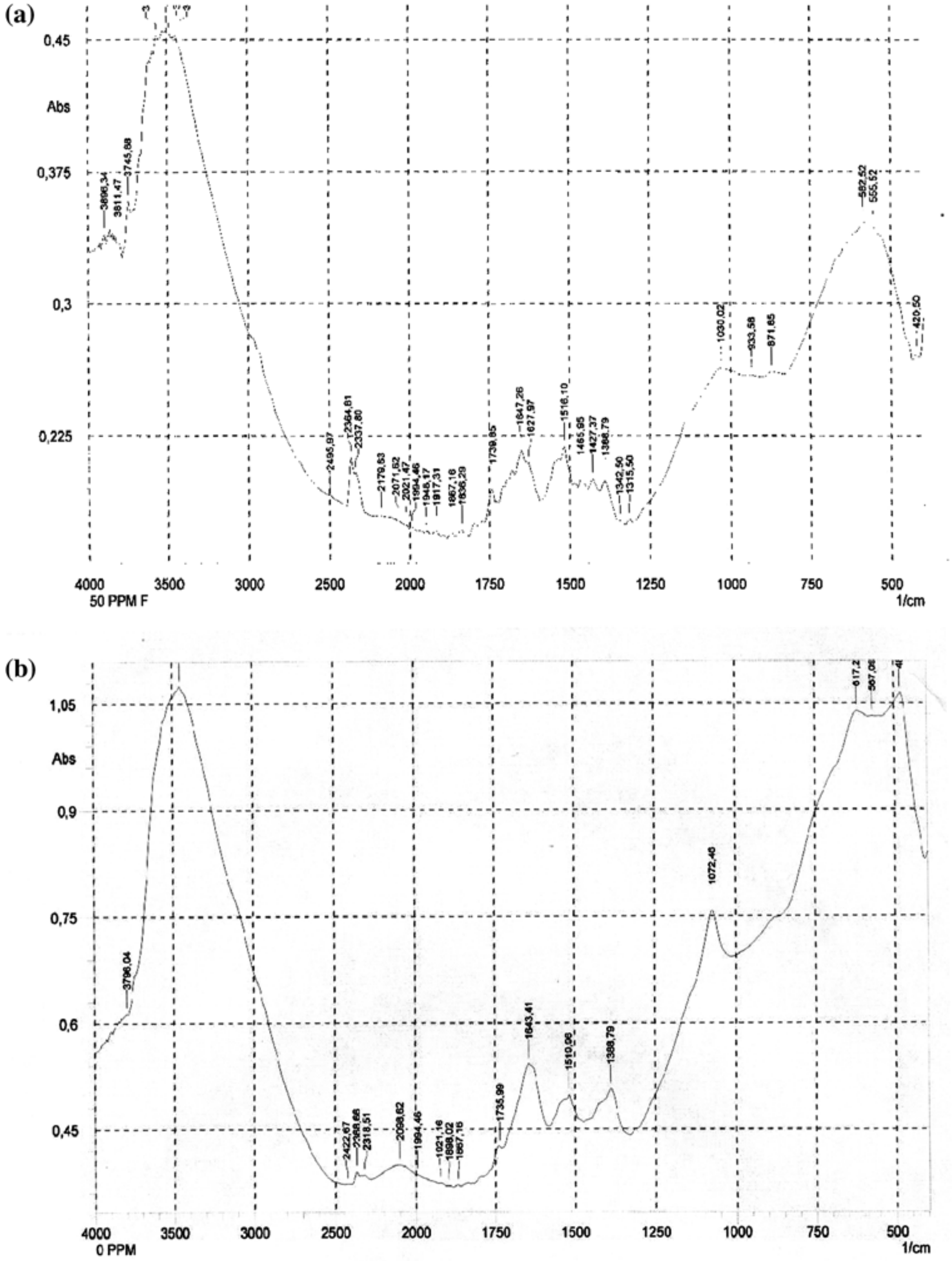

Fig. 8. FTIR spectra of EC formed sludge in absence (a) and presence (b) of fluoride, initial fluoride concentration, 50 mg/L; initial $pH_0 = 7$.

Fig. 8, it can be concluded that FTIR spectrum (a) shows some spectroscopic changes. This is probably due to the presence of fluoride ions, which suppose that the OH^- of $Al(OH)_3$ was partially replaced by F^- ions.

Identical FTIR observations were obtained by previous works [16], when eliminating fluoride by alum-based coagulant. This was explained by the fact that hydroxide ions OH^- of aluminum hydroxide and fluoride ions F^- in solution have similar dimensions, and thus, F^- ions may undertake isomorphous exchanges to replace OH^- ions. From this analysis, it may be confirmed that fluoride was linked to form precipitated aluminum hydroxide complexes.

Thus, we may say from the above characterization results that $Al(OH)_3$ precipitates that the formation is enhanced in these pH conditions (pH 7) have large surface areas, which are beneficial for a rapid adsorption of soluble compounds like fluorides.

In the literature, two main mechanisms for fluoride removal were proposed, adsorption and co-precipitation [17,18]:

Adsorption on $Al(OH)_3$:

$$\mathrm{Al}_n(\mathrm{OH})_{3n(\mathrm{s})} + \mathrm{mF}^-_{(\mathrm{aq})} \rightarrow \mathrm{Al}_n\mathrm{F}_m(\mathrm{OH})_{3n-m(\mathrm{s})} + \mathrm{mOH}^-_{(\mathrm{aq})} \quad (7)$$

Co-precipitation:

$$\mathrm{nAl}^{3+}_{(\mathrm{aq})} + (3n-m)\mathrm{OH}^-_{(\mathrm{aq})} + \mathrm{mF}^-_{(\mathrm{aq})} \rightarrow \mathrm{Al}_n\mathrm{F}_m(\mathrm{OH})_{3n-m(\mathrm{s})} \quad (8)$$

Hence, the $Al(OH)_3$ floc is believed to adsorb F^- strongly, as shown by Eq. (7). The sludge characterization results confirmed the adsorption pathway in which the final product is aluminum fluoride hydroxide complex $Al_nF_m(OH)_{3n-m}$.

4. Conclusion

This study revealed that EC is an efficient technique for polishing treatment of HF wastewaters. The EC shows to be a good alternative to conventional coagulation–flocculation process.

The study of different involved parameters indicated that:

Among studied anode–cathode pairs, Aluminum–Aluminum (Al–Al) pair gives best results in terms of fluoride removal.

Current density is the most important parameter. Increasing current density enhances fluoride removal.

Increasing electrolysis time is favorable for fluoride removal.

The best efficiencies are obtained in initial pH media between 5 and 7.

The weaker is the initial fluoride concentration; the easier is its treatment.

In presence of nitrate anions, the highest EC fluoride removal is obtained.

References

[1] F. Shen, X. Chen, P. Gao, G. Chen, Electrochemical removal of fluoride ions from industrial wastewater, Chem. Eng. Sci. 58 (2003) 987–993.

[2] N. Drouiche, N. Ghaffour, H. Lounici, M. Mameri, Electrocoagulation of chemical mechanical polishing wastewater, Desalination 214 (2007) 31–37.

[3] N. Kabay, Ö. Arar, S. Samatya, Ü. Yüksel, M. Yüksel, Separation of fluoride from aqueous solution by electrodialysis: Effect of process parameters and other ionic species, J. Hazard. Mater 153 (2008) 107–113.

[4] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.

[5] Y.S. Yildiz, Optimization of Bomaplex Red CR-L dye removal from aqueous solution by electrocoagulation using aluminum electrodes, J. Hazard. Mater. 153 (2008) 194–200.

[6] C. Escobar, C. S-Salazar, M. Inés Tora, Optimization of the electrocoagulation process for the removal of copper, lead and cadmium in natural waters and simulated wastewater, J. Environ. Manage. 81 (2006) 384–391.

[7] J. Ge, J. Qu, P. Lei, H. Liu, New bipolar electrocoagulation–electroflotation process for the treatment of laundry wastewater, Sep. Purif. Technol. 36 (2004) 33–39.

[8] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, Decolorization of basic dye solutions by electrocoagulation: An investigation of the effect of operational parameters, J. Hazard. Mater B129 (2006) 116–122.

[9] S. Aoudj, A. Khelifa, N. Drouiche, M. Hecini, H. Hamitouche, Electrocoagulation process applied to wastewater containing dyes from textile industry, Chem. Eng. and Process: Process Intens. 49 (2010) 1176–1182.

[10] A.E. Greenberg, L.S. Clesceri, A.D. Eaton, Standard methods for the examination of water and wastewater, 18th ed., APHA, Washington, DC, 1992.

[11] K. Bensadok, N. El Hanafi, F. Lapicque, Electrochemical treatment of dairy effluent using combined Al and Ti/Pt electrodes system, Desalination 280 (2011) 244–251.

[12] A. Gadd, D. Ryan, J. Kavanagh, A.-L. Beaurain, S. Luxem, G. Barton, Electrocoagulation of fermentation wastewater by low carbon steel (Fe) and 5005 aluminium (Al) electrodes, J. Appl. Electrochem. 40 (2010) 1511–1517.

[13] M.Y.A. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, J. Hazard. Mater. B 114 (2004) 199–210.

[14] N. Mameri, A.R. Yedou, H. Loucini, D. Belhocine, H. Grib, B. Bariou, Defluoridation of septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrodes, Water Res. 32 (1998) 1604–1612.

[15] Q. Zuoa, X. Chen, W. Li, G. Chen, Combined electrocoagulation and electroflotation for removal of fluoride from drinking water, J. Hazard. Mater. 159 (2008) 452–457.

[16] S. Aoudj, N. Drouiche, M. Hecini, T. Ouslimane, B. Palaouane, Coagulation as a post-treatment method for the defluoridation of photovoltaic cell manufacturing wastewater, Procedia Eng. 33 (2012) 111–120.
[17] S. Maliyekkal, S. Shukla, L. Philip, I. Nambi, Enhanced fluoride removal from drinking water by magnesia-amended activated alumina granules, Chem. Eng. J. 140 (2008) 183–192.
[18] N. Drouiche, S. Aoudj, M. Hecini, N. Ghaffour, H. Lounici, N. Mameri, Study on the treatment of photovoltaic wastewater using electrocoagulation: Fluoride removal with aluminium electrodes: Characteristics of products, J. Hazard. Mater 169 (2009) 65–69.