Contribution of the electrocoagulation method in the removal of fluorine ions from aqueous solutions

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ABSTRACT

Photovoltaic technology has experienced a huge global economic boom in recent decades and a growing trend is expected in the future. This technology consists of the application of a number of processes including growth, oxidation, doping, metallization, etc. In order to reduce the fluoride content in the water below a threshold value that complies with the standards of industrial discharges or water intended for human consumption, various treatment techniques have been implemented. In this respect, electrocoagulation (EC) has been chosen in this study because of its performance compared to other methods. Wastewaters from surface treatment of silicon wafers are rich in fluoride and the lime precipitation is insufficient to comply with environmental standards. In this work, the EC technique, with Fe anodes, was used as an alternative for water purification. By coupling electroflotation to the electrocoagulation in the same cell, the separation of solid/liquid was significantly improved. To study the process performance, tests on the effect of the operational parameters such as current intensity, initial pH, nature of supporting electrolyte and its concentration were carried out on synthetic solutions. The optimal values are: pH \(_o\) = 4; current = 1.4 A and [NaCl] = 2 g/L. The removal efficiency of 62% was reached starting from an initial concentration of 35 mg/L. A total clarification of the synthetic solution was also obtained.

Keywords: Electrocoagulation; Electroflotation; Silicon wafers; Iron; Water treatment; Fluorine

1. Introduction

The increased agro-industrial activities have generated increasing pressure on the planet's freshwater reserves. This accelerated development is often accompanied by large-scale pollutions of the atmosphere and water, thus posing a real threat to the environment. Often the chemicals in wastewater are difficult to biodegrade, whether they are stable organics or heavy metals. The absence or insufficiency of treatment systems has therefore led to the accumulation of pollution during the water cycles. Environmental protection has become a major economic stake because all the countries of the world are concerned about the protection of freshwater resources. One of the major challenges facing humanity today is providing safe drinking water to the vast majority of people around the world, and the need for clean water is particularly critical in the Third World. Rivers, canals, estuaries and other water bodies are constantly polluted by the indiscriminate discharge of industrial effluents and the reuse of wastewaters has become an absolute necessity. There is, therefore, an urgent need to develop innovative, efficient and inexpensive purification techniques. In Algeria, after quality and productivity, the environment constitutes the third industrial challenge to be taken up, faced with increasingly drastic environmental regulations. The photovoltaic (PV) industry is one of the economic sectors that has grown rapidly in recent times. This new technology
that can contribute to energy needs to be compatible with the concept of sustainable development. The manufacturing processes involve physicochemical reactions, with numerous chemicals, liquid or gaseous, more or less toxic (HF, ammonia, etc.). Among the many pollutants, HF poses a serious threat; it is at the heart of the photovoltaic wafer industry and is used in wafer stripping operations. This comes down to its ability to attack silicon oxide and turn it into soluble compounds. Fluoride concentrations in the range (500–2,000 mg/L) are commonly encountered in the wastewater from the PV industry [1] and the contamination has adverse health effects. Given its high toxicity, industrial F– discharges are strictly regulated. The tolerated limit is the water standards is restricted at 15 mg/L for industrial aqueous discharges. Currently, the most efficient and inexpensive way to reduce high F– level is lime precipitation. However, defluorination by this technique does not allow to reach a residual F– concentration lower than that required by the standards. In addition, the difficulty of sedimentation of the fine particles of produced fluorite (CaF₂) leads to relatively a persistent turbidity; a refining treatment is then necessary and many techniques have been proposed, including the coagulation–flocculation, adsorption [2–11], photocatalysis [12], reverse osmosis, etc. In addition, promising techniques based on electrochemical technology, and which do not require additional chemical agents, are being developed. The electrocoagulation (EC) [13,14] makes it possible to considerably overcome the drawbacks of conventional purification techniques, developed before the twentieth century with however limited success and popularity; the anodes were then formed by Fe and Al plates. In the fifties, the first application of EC concerned the treatment of drinking water [15]. It is currently the subject of research for the treatment of a variety of polluted effluents [16–21], as well as waters containing fluorinated compounds [22,23], textile dyes [24], nitrates [25] and phosphorus [26]. Therefore, several studies, devoted to the elimination of fluoride by EC, led to the choice of aluminum as the working electrode. In this study, EC using Fe electrodes was examined as a post-treatment. The objective of this work is to study the F– elimination from the photovoltaic cell manufacturing industry by the EC process. For, the EC performance, tests on the effect of the operational parameters such as the current intensity, initial pH, nature of supporting electrolyte and its concentration were carried out on synthetic solutions in batch mode. A combination of the two techniques (EC and EF) in a single cell constitutes the logical continuation of this work which contributes to facilitate flock flotation on the one hand and minimizing energy consumption on the other hand.

2. Analytical methods

2.1. Potentiometric analysis of fluorides

The concentration of F– is measured by the standard ionometric method, using a fluoride ion-selective electrode (PF4L Tacussel) associated with a saturated calomel electrode as a reference electrode. A calibration graph was established in order to accurately evaluate the F– concentration in a solution by linear interpolation. To prevent the F– complexation by Fe²⁺ and Ca²⁺ ions, a buffer solution was added to the aliquots before titration. This analysis is carried out after filtration (50% by volume) of the buffer solution and reading the potential. The analysis of the sample is done in the same way as for the standards.

2.2. PH measurement

The pH is measured with an inolab level 1 pH meter, calibrated before with standard buffer solutions of pH 4, 7, 10 with a precision of ±0.02 units at 20°C. The pH electrode is immersed in the effluent in the middle of the cell during the electrolysis and the values are read after stabilization which in our case occurs after 5 min. The initial pH was varied between 4 and 8 using HCl and NaOH solution (0.1 N).

3. Electrocoagulation methods

3.1. Principle of electrocoagulation

The EC technique is based on the principle of soluble anodes which imposes an electrical current (or potential) between two electrodes, in our case, Fe and Al immersed in an electrolyte contained in a reactor to generate, in situ, ions Fe²⁺, Fe³⁺, Al³⁺ capable of producing a coagulant in solution and causing coagulation–flocculation of the pollutants that we want to eliminate. The electrolysis can also remove oxidizable or reducible species from various effluents. The electric field generates a movement of ions and brings together the suspended matter in the form of flocs which are removed by a conventional physical process (settling, flotation, and filtration). Fig. 1 illustrates the principle of the EC process which involves several physical and chemical phenomena that use consumable (sacrificial) electrodes to deliver ions into the effluent to be treated. Three successive stages are involved during the EC process:

- Formation of coagulants by electrolytic oxidation of the sacrificial electrode.
- Destabilization of contaminants and particulate suspensions.
- Aggregation of the destabilized phases to form the flocs.

![Fig. 1. Principle of the electrocoagulation process.](image-url)
3.2. Electrocoagulation mechanism

The mechanism of destabilization of contaminants and particulate suspensions can be summarized as follows:

- Compression of the diffuse layer around the charged species by interactions with ions generated by oxidation of the sacrificial anode.
- Neutralization of the charge of ionic species present in the waste to be treated against the ions produced by electrochemical dissolution of the sacrificial anode. These ions reduce the electrostatic repulsion between particles until the Van der Waals attractive forces predominate, thus causing the coagulation process.
- The flocs formed following coagulation create sludge which traps and connects the colloidal particles remaining in the aqueous medium.

When the minimum solubility of Fe(OH)\(_3\) and Fe(OH)\(_2\)(s) is reached, insoluble precipitates are formed which interact with the pollutants by adsorption. In addition, such precipitates lead to the formation of large flocs, commonly called “sweep flocs” which generate a veil of mud and traps the particulate and colloidal polluting particles in the precipitate flocs.

4. Experimental batch study

The experiments were carried out with synthetic solutions obtained by dissolving NaF in distilled water. To simulate the photovoltaic effluent after neutralization, Ca(OH)\(_2\) lime was used to precipitate the F\(^-\) ions in solution. After adding the lime, the solution was stirred for 30 min. (optimized time) to homogenize the species in order to have a maximum of precipitation. The initial fluoride concentration [F\(^-\)]\(_0\) vary between 30 and 40 mg/L. The F\(^-\) removal efficiency is expressed in terms of the removal rate R(%) which is given by:

\[
R(\%) = \left(\frac{[F^-]_0 - [F^-]_t}{[F^-]_0}\right) \times 100 \tag{1}
\]

where [F\(^-\)]\(_0\) is the concentrations at the time (mg/L); all tests were realized in batch mode. After starting the electrolysis, the stopwatch is started, the pH is checked (reading every 5 min) and periodic samples are taken regularly (every 15 min) using a syringe (5 mL) to monitor F\(^-\) concentrations. Immediate filtration using a syringe filter (0.2 µm pore diameter) was necessary for each sample to remove the flocs and solid species that adsorb F\(^-\) ions and distort the concentration after sampling.

5. Results and discussion

The lime precipitation operations took place at moderate speed. In order to work under the same experimental conditions and to have stable final F\(^-\) concentrations, we will optimize the precipitation time, which expresses the time necessary to reach the equilibrium. To apply it to all the tests preceding the treatment, this time makes it possible to have the concentrations [F\(^-\)] close or equal, which gives the results with a better reproducibility. The operating conditions under which the precipitation was carried out are gathered in Table 1.

5.1. Determination of the precipitation time

The evolution of the residual F\(^-\) concentration allowed us to determine the time required for the precipitation. The sources of calcium usually used to precipitate fluorides in the form of fluorate (CaF\(_2\)) are lime Ca(OH)\(_2\), calcium chloride CaCl\(_2\) and calcium sulfate CaSO\(_4\), the reactions involved are as follows:

\[
2F^- + Ca(OH)_2 \rightarrow CaF_2 + 2OH^- \tag{2}
\]

\[
2F^- + CaCl_2 \rightarrow CaF_2 + 2Cl^- \tag{3}
\]

\[
2F^- + CaSO_4 \rightarrow CaF_2 + SO_4^{2-} \tag{4}
\]

When the reagents are in stoichiometric quantities, the thermodynamic calculations give a solubility of CaF\(_2\), equal to 16 mg/L at 20°C, and 8.18 mg/L of [F\(^-\)]; the solubility product of fluorate Kps (20°C) = 4 \times 10\(^{-11}\) is taken from the study of Jane Huang and Liu [1] and Abbas and Trari [12]. However, in actual effluents, the F\(^-\) concentrations are higher than those theoretically predicted and lie between 20 and 60 mg/L. This is mainly due to the high ionic strength and slow nucleation [26]. Therefore, the formation of the precipitate is a relatively slow process that depends on a number of factors such as the stirring time and agitation speed. The latter plays a major role in the precipitation, as it controls the mass transfer. A low speed causes slow kinetics while a vigorous stirring generates very fine F\(^-\) particles which pose a problem of separation.

Examination of Fig. 2 shows that the precipitation time is a determining parameter and that the increase in the residence time of the reagents causes a reduction in the final residual F\(^-\) contents. Under these working conditions, the time required for the precipitation is almost 30 min. From this time, the F\(^-\) concentration begins to stabilize and a plateau region characterizes the shape of the obtained curve obtained. This time is applied in the protocol for preparing the solutions of all the experiments.

5.2. Effects of F\(^-\) concentration on the human health

Ingestion of fluoride is necessary for human metabolism. However, a deficiency or an excess of fluoride causes
undesirable effects. Most foods contain fluorides, like fish and tea, and depend on the geographical location, and therefore on the variations in the chemical composition of water, the main vector of fluoride intake perhaps, that is, water consumed, or feed. The F⁻ ion is quickly incorporated into teeth and bones. At high doses (a few hundred mg/L), F⁻ can cause pathological conditions such as hemorrhagic gastroenteritis, acute nephritis and various lesions in the liver and heart which can sometimes lead to death. Table 2 summarizes the consequences of human health according to the limit of fluorine in the human body.

5.3. Determination of the electrolysis time

The electrolysis time is a crucial important parameter, it not only determines the time necessary for a maximum elimination of pollutants, but it also affects the energy consumption which is a decisive economic factor for the profitability of the process on an industrial scale. The efficiency of pollutant removal depends on the generation of iron ions at the anode. Thus, a longer electrolysis time will result in a high rate of production of iron hydroxides which in turn are responsible for the coagulation of pollutants. Fig. 3 illustrates the variation of the rate of F⁻ removal as a function of time. One can notice that the kinetic of the EC is faster in the range (0–90 min), and increase very slowly in the region (90–140 min). Beyond 90 min a kind of plateau appears. Therefore, 90 min was chosen to compromise treatment efficiency and energy consumption.

5.4. Effect of current intensity on the removal efficiency of F⁻ ions

In the EC process, the main reactant is the electrical charge flowing through the circuit, so controlling the electricity is a key parameter in the EC process [27]. The current imposed during the treatment plays a determining role for the pollutant reduction and the turbidity, as well as for the treatment time and is responsible for the reactions kinetic which takes place onto the electrodes. While studying this parameter (Fig. 4), we carried out a series of tests applying the following currents: 0.6, 1.0 and 1.4 A, maintaining the other operating parameters constant. The results show that the removal efficiency increased rapidly with increasing the current intensity (I = 1.4 A, R(%) = 85; I = 1.0 A, R(%) = 46; I = 0.6 A, R(%) = 30). The higher the current, the faster and more significant the F⁻ elimination.

The variation in current intensity (Fig. 4) shows that the best removal rates are achieved with the highest intensities, at faster kinetics. This proportionality is explained by the acceleration of the reactions on the electrodes when the intensity augments, thus decreasing the processing time. At the anode, a strong dissolution leads to the release of a large quantity of metal cations which play the role of coagulating agents [28] and form various metal hydroxides favorable to the F⁻ elimination. On the other hand, they increase the ionic force exerted on the particles, which destabilizes the latter, thus giving a better elimination. Likewise, at the cathode, the rate of production of H₂ bubbles augments and increases the probability of attachment to the particles and flocs. In addition, their size decreases [29], providing a large surface area favorable to their attachment to the particles. All of these effects are beneficial for electroflocculation removal and the results are in good agreement with those observed elsewhere [30]. However, high intensity is undesirable, since it causes an intensive...

Table 2

<table>
<thead>
<tr>
<th>Concentration in fluorides (mg/L)</th>
<th>Health effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.5</td>
<td>Cavities</td>
</tr>
<tr>
<td>0.5–1.5</td>
<td>Optimal dose to prevent cavities</td>
</tr>
<tr>
<td>1.5–4</td>
<td>Problems with the dental framework</td>
</tr>
<tr>
<td>&gt;4</td>
<td>Bone diseases</td>
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Fig. 2. Effect of time on lime precipitation, stirring speed V = 100 rpm.

Fig. 3. Effect of electrolysis time on fluoride removal: I = 0.6 A; [NaCl] = 2 g/L; pH = 4; [F⁻]₀ = 35 mg/L.

Fig. 4. Effect of time on lime precipitation, stirring speed V = 100 rpm.
flow of bubbles by the competitive effect which affects the accumulation and stability of the sludge on the surface.

5.5. Effect of initial pH on the removal efficiency of fluorine ions

The initial pH is known to be one of the primary factors controlling the EC performance [31]. It is a crucial parameter that conditions the presence of specific forms of iron complexes. To study the pH influence on the F– removal, we performed a series of tests at pH: 4, 7 and 9, keeping the other parameters constant. The kinetic results (Fig. 5) clearly show that the best removal rates are obtained for an acidic pH.

The basic medium disadvantages the F– removal efficiency while the optimum initial pH ensuring better defluorination efficiency was observed at pH 4 with an abatement of 45%. These results can be explained by the fact that Fe(OH)2+, Fe(OH)3+ and Fe(OH)4– species favorable to coagulation are present under acidic conditions by hydration of Fe3+ ions. The reactions concerned are [32]:

\[
\begin{align*}
Fe^{3+} + H_2O &\rightarrow Fe(OH)^{2+} + 2H^+ \quad (5) \\
Fe^{3+} + 2H_2O &\rightarrow Fe(OH)_2^+ + 2H^+ \quad (6) \\
Fe^{3+} + 3H_2O &\rightarrow Fe(OH)_3^- + 2H^+ \quad (7)
\end{align*}
\]

The results obtained are in agreement with those found by certain authors [33,34].

5.6. Evolution of pH during electrocoagulation

The change in pH during the EC treatment was studied for three current intensities; 0.5, 1 and 1.5 A (Fig. 5) in order to better perceive the phenomenon, as well as the effect of the current intensity on this evolution. The pH level shows a rapid increase at the start of treatment followed by a stabilization under the buffering effect of the electrocoagulation. We also note that this increase is all the more important as the current intensity is high as observed by Arslan-Alaton et al. [35]. This increase in pH is due to the production of OH– ions at the cathode, so a high intensity accelerates this production which leads to a strong and steep release of OH– ions. A previous study showed that the pH remains roughly neutral when Al anode is used while with Fe anode, the pH even rose from 7 to over 11 [36].

5.7. Effect of the nature of the supporting electrolyte

Fluoride contaminated wastewater most often contains other anions such as Cl–, SO4^2–, CO3^2– and NO3–. These anions, at different concentration, come from the products used in the silicon manufacturing processes. Furthermore, in the electrochemical processes, the soluble electrolyte is known for its important role in ensuring good conductivity by supplying ions to the solution. For the EC process, its role is not limited and increases the ionic concentration (C) which thus results in the narrowing of the double layer which varies as C^–1/2, thus allowing better coagulation.

Therefore, we looked at three types of electrolytes having the same Na+ cation, namely NaCl, Na2SO4 and Na2CO3. The experiments were carried out under the optimum conditions for the current intensity and initial pH, established above. The results (Fig. 6) show that the nature of the electrolyte has a significant influence on the kinetics of fluorine elimination. Indeed, the defluorination process is more significant by using NaCl with rapid kinetics in comparison with those with the other electrolytes.

The removal rates differ with the nature of the electrolyte, a better rate of 45% is obtained with NaCl while with Na2SO4 and Na2CO3 the removal rates reach respectively 39.8% and, 36.7%. This former can be explained by the effect of the Cl– ions on the electrodes by avoiding a possible passivation or formation of an impenetrable passive film of iron oxide or calcium carbonate on their surface which affects the anodic dissolution [32].

![Fig. 4. Effect of current intensity on fluoride removal: \(I = 0.6\ A; [NaCl] = 2\ g/L; pH = 4; [F^-]_0 = 35\ mg/L\).](image)

![Fig. 5. Evolution of the pH over time: \(I = 0.6\ A; [NaCl] = 2\ g/L\).](image)
5.8. Effect of electrolyte concentration

The salt in solution, by its content, affects the efficiency, the cell voltage and the consumption of electrical energy [15]. To study the influence of the salinity of the solution on the EC kinetics, we performed a series of tests using NaCl. Five concentrations were studied (0.25, 0.5, 1, 2, and 5 g/L) while keeping the optimal operating conditions that have been established above. Fig. 7 illustrates the dependence of the F\(^-\) removal rate on the carrier electrolyte dose.

The influence of the electrolyte concentration was studied by adding the appropriate amounts of NaCl and shows that the effectiveness of the treatment is optimal for a concentration of 2 g/L with a rate of 45%. This result agrees with the literature [12] and shows that when the electrolyte concentration increases from 0.25 to 2 g/L, the elimination rate augments from 35% to 46%. The advantage of increasing the salt concentration is to augment the electrical conductivity, to this advantage is added the increased ionic strength as previously indicated. A test was carried out for a NaCl concentration equal to 5 g/L, which resulted in a decrease of F\(^-\) removal efficiency with an abatement of 36.8%, that is, a decrease of 8% compared to the optimal concentration (2 g/L), the same result is obtained in the literature [37,38].

6. Conclusion

This study showed that electrocoagulation is an interesting alternative for the treatment of effluents from the surface of silicon wafers, the electricity and the economic ratio are very attractive. In fact, an elimination rate of 62% corresponds to a final fluoride concentration of 13.74 mg/L which is below the water standards.

In addition, the electrocoagulation allowed us to achieve a total clarification of the synthetic solution without any settling at the bottom of the reactor. This would allow the effluent to be discharged without any danger to nature and would minimize cell maintenance operations.

The results showed also that the intensity of the applied current, initial pH of the medium, the nature of the supporting electrolyte and its concentration strongly influence the effectiveness of the EC treatment. The effect of current intensity indicated that the fluoride removal is very sensitive to this parameter. The rate of fluoride elimination is greater and the time of treatment is shorter at high intensity and the best elimination rate was obtained with the current of 1,400 mA. In addition, a high current is undesirable for the system, since it causes an intensive flow of bubbles by competitive effect, which impairs the good accumulation and stability of sludge at the surface.

The initial pH has shown that the best F\(^-\) elimination is obtained at acidic pHs with an optimal pH equal to 4. Lower pHs have not been studied to avoid the risk of attack on the glass by HF.

This study demonstrated the remarkable effect of the nature of the supporting electrolyte and its concentration. NaCl seems to be the best electrolyte, its efficiency is due to the power of chloride which prevents any possible passivation. The increase of its concentration is favorable up to a threshold of 2 g/L, above which a decrease in efficiency is observed.

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