Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1095120

57 (2016) 18398–18405
August

Taylor & Francis
Taylor & Francis Group

Removal of fluoride and turbidity from semiconductor industry wastewater by combined coagulation and electroflotation

S. Aoudj[a,b,*], A. Khelifa[b], N. Drouiche[a], M. Hecini[a]

[a] *CRTSE-Division CCSM-No 2, Bd Dr. Frantz FANON-P.O. Box 140, Alger sept merveilles 16038, Algeria, Tel. +213 21 279880, ext. 172; Fax: +213 21 433511; emails: aoudjsalah@yahoo.fr (S. Aoudj), nadjibdrouiche@yahoo.fr (N. Drouiche), hecinimouna@yahoo.fr (M. Hecini)*

[b] *Laboratoire de génie chimique, Département de Chimie Industrielle, Université Saâd Dahlab de Blida, B.P. 270, Route de Soumâa, 09000 Blida, Algérie, email: khelifaab@hotmail.com (A. Khelifa)*

Received 27 November 2014; Accepted 26 August 2015

ABSTRACT

Reduction of toxic dissolved fluoride and CaF_2 nanoparticle pollution is a critical environmental problem for the semiconductor industry. In this study, suspended matter and fluoride are simultaneously eliminated by combining coagulation and electroflotation. The EF cell was equipped with DSA titanium coated with ruthenium oxide (Ti/RuO_2) as anode and stainless steel as cathode. High turbidity removal efficiency is achieved by using EF as a separation technique. The effect of the following parameters: electrolysis time, coagulant concentration, initial pH, nature of neutralizing salt and current intensity was studied. Removal efficiencies of both fluoride and CaF_2 nanoparticles are satisfactory. Under optimum conditions, the solid–liquid separation efficiency is about 97% in terms of turbidity removal which corresponds to a residual turbidity of 4.4 NTU complying with the standard limit (5 NTU), while fluoride efficiency removal may reach 73% corresponding to 10 mg/L, which is below the environmental recommendations.

Keywords: Semiconductor wastewater; Fluoride; CaF_2 nanoparticles; Coagulation; Electroflotation

---

1. Introduction

In semiconductor industry units, such as photovoltaic cell manufacturing and electronics plants, a large quantity of hydrofluoric acid is currently used. It is employed for wafer etching and quartz cleaning operations [1]. The generated acid fluoride-containing wastewaters are characterized by low pH and fluoride concentrations more than 1,000 mg/L [1,2]. The direct discharge of such solutions may represent a huge threat for the environment. The World Health Organization recommended 1.5 mg/L as a limit for fluoride concentration in drinking water. In Algeria, the maximum discharge limit is 15 mg/L in industrial effluent.

The most commonly used method for fluoride removal is precipitation using calcium salt, such as lime or calcium chloride. Fluoride reacts with calcium to form calcium fluoride precipitate as follows:

$$Ca^{2+}_{(aq)} + 2F^{-}_{(aq)} \leftrightarrow CaF_{2(s)} \qquad (1)$$

---

*Corresponding author.

When fluoride and calcium ions are in stoichiometric amounts, solubility calculations reveal that the residual fluoride is about 8.18 mg/L [3,4]. However, in real wastewater, fluoride concentrations are higher than those predicted theoretically and may be between 20 and 60 mg/L [5,6]. Furthermore, the formation of the CaF_2 precipitates results in very fine colloidal particles which settle very slowly [3]. The high turbidity level in the effluent limits the reuse/recycling of water for further usage. Thus, a polishing step is needed to lower the suspended solids and fluoride concentrations after calcium precipitation. Various treatment technologies, such as coagulation, electrocoagulation–flotation [7–9], membrane separation [10], fluidized-bed precipitation [11] have been proposed.

In practice, the most recently applied method consists of coagulation followed by flocculation and sedimentation [12]. However, some limitations are reported by plant engineers such as production of sludge causing disposal problem in addition to poor settling characteristics of the flocks which implies large decantation tanks and large land area are required[3,12–14]. Therefore, an alternative separation process to be associated with coagulation is needed. Filtration and membrane technology were proposed to improve treated wastewater quality and to meet reuse criteria [15]. However, the particle removal efficiency for the filtration technique is significant only if the equivalent particle size is greater than 20 μm. Membrane processes are becoming very popular, but the fouling problems and high cost related to this technology limit its wide use [15].

Electroflotation (EF) has received growing interest [16,17]. It is a highly versatile technique. EF units are small and compact and require lower maintenance and running costs compared to other flotation units. The electroflotation technique principle is based upon the generation of hydrogen and oxygen gases during the electrolysis of water. The main reactions taking place at the electrodes during EF are as follows:

$$\text{At the anode}: \ 2H_2O \rightarrow 4H^+ + O_2 + 4\acute{e} \tag{2}$$

$$\text{At thecathode}: \ 4H_2O + 4\acute{e} \rightarrow 2H_2 + 4OH^- \tag{3}$$

The gas bubbles formed on the electrode surface make contact with particles in suspension and the particle–bubble combination rises to the surface where the suspended pollutant is removed by a skimming method [14]. Compared with conventional flotation, electroflotation has many advantages. Firstly, its fine bubbles which are uniformly dispersed thus increasing the contact area between the suspended particle and bubble, making the clarification efficient and fast. Secondly, it generates less sludge. Thirdly, it offers the possibility of automation and easy operation by adjusting the electrical current [12,18–20].

A few works have investigated EF in the treatment of wastewater containing dispersed ultra-fine particles. They report that efficient liquid–solid separation is obtained when a coagulating agent is added to improve the flotation. The coagulation–electroflotation technique was successfully applied in the removal of oil from oil/water emulsions [14], diluted cutting oil emulsions [21], effluents from cardboard industry [22], wastewaters of paper industry [23] and textile effluent containing reactive dyes [24].

The aim of this work is to combine coagulation with electroflotation as a finishing treatment of acid wafer processing effluents after the lime precipitating step. The EF experiments were carried out in an electrolytic cell equipped with insoluble electrodes. The effect of operating parameters such as electrolysis time, coagulant concentration, initial pH, nature of neutralizing salt and current intensity on the performance of the electrolytic cell was examined.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

The precipitation and coagulation tests were performed in a 1.5 L glass beaker equipped with a magnetic stirrer. The batch electroflotation tests were carried out in an electrolytic cell made of plexiglas (14 cm × 8 cm × 42 cm). The dimensionally stable anode (DSA®) was a sheet of titanium coated with ruthenium oxide (Ti/RuO_2). The Ti/RuO_2 anodes show high catalytic activity for O_2 evolution, high stability to anodic corrosion and excellent mechanical stability [25]. The cathode was of stainless steel. Stainless steel is of low cost, chemically resistant and it gives rise to tiny bubbles [17,26]. The two electrodes, of (5 cm × 13 cm) dimensions and separated from each other by 1 cm, are mounted horizontally at the bottom of the reactor (Fig. 1). The thickness of the electrodes was 3 and 4 mm for anode and cathode sheets respectively. The Ti/RuO_2 plate was placed underneath and the stainless steel screen (with 65 holes, 5 mm in diameter, representing almost 39% of the whole cathode area) was placed above. Such an arrangement allows a better uniform dispersion of the electrogenerated bubbles and permits the flotation of precipitate flocs to the top [27]. The electrodes were connected to a digital DC power supply (Metrix AX502, 0–2.5 A

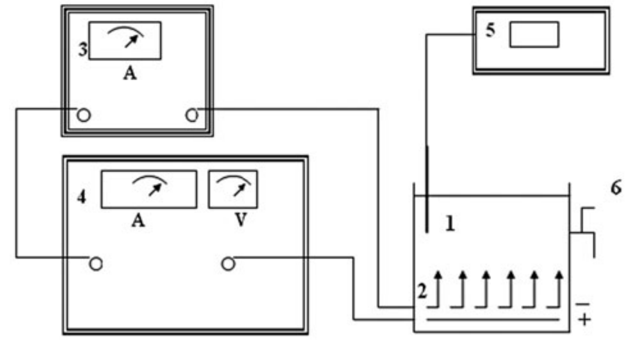

Fig. 1. Electroflotation set-up diagram.
Notes: (1) EF cell, (2) electrodes, (3) ammeter, (4) DC power supply, (5) pH meter and (6) sample tap.

and 0–30 V). An ammeter (Chauvin–Arnoux C.A 401) was used to monitor the current during the ECF process.

2.1.2. Procedure

Synthetic solutions were prepared by mixing known amounts of sodium fluoride NaF and calcium hydroxide $Ca(OH)_2$ (or occasionally $CaCl_2$) with distilled water in order to simulate the semiconductor wastewater after calcium precipitation. This involves rapid mixing at 400 rpm for 1 min, followed by a mixing at 200 rpm for 30 min. The used coagulant is aluminium sulphate ($Al_2(SO_4)_3{\cdot}18H_2O$). Various amounts of coagulant were added to the synthetic solution. The mixed liquor was firstly stirred for 20 min to allow the coagulation reaction to proceed and the pH value was adjusted to a desired level using 0.1 M NaOH and 0.1 M HCl solutions. The prepared solution is then introduced to the EF cell and the flotation step starts. The treatment duration was fixed at 60 min for all experiments. The pH was continuously measured by immersing the pH meter electrode in the treated solution. The turbidity of drawn samples was instantaneously measured without a subsequent decantation. For fluoride analysis, samples were first filtered by means of a membrane filter (0.22 μm) to remove tiny CaF_2 and aluminium compounds. The removal efficiency was calculated based on the following formula:

$$R\ (\%) = \frac{(C_0 - C)}{C_0} \times 100 \tag{4}$$

where C_0 and C are the initial concentration and concentration at time t of the studied parameters, respectively.

2.2. Analysis

A selective ion sensor electrode (HACH (Sension1)) was used to determine the fluoride concentration according to the standard method [28]. T1SAB buffer [58 g of NaCl, 57 mL of glacial acetic acid, 4 g of 1,2 cyclohexylenediaminetetraacetic acid(CDTA), 125 mL of 6 N NaOH were dissolved and stirred in 1000 mL of distilled water until pH 5.3–5.5 was reached] was added to the samples in the ratio 1:1. The TISAB was added in order to regulate the ionic strength of samples and standard solutions, to adjust the pH (5.3–5.5) and also to avoid interference from the Al^{3+} and Ca^{2+} ions. The turbidity was measured as nephelometric turbidity unit (NTU) using the turbidimeter (HANNA model HI7027). The pH values were determined using Sension1 pH-meter (HACH).

3. Results and discussion

3.1. Effect of coagulant dose

After calcium precipitation, both soluble fluoride ions and CaF_2 particles are present in the semiconductor wastewater. These pollutants can be removed simultaneously by coagulants. In order to study the effect of coagulant concentration on the treatment efficiency, different coagulant doses ranging from 0 to 320 mg/L were used. It may be observed from results depicted in Fig. 2 that in the absence of aluminium coagulant, the turbidity removal was only 36%. This may be explained by the CaF_2 particle size which makes the particle–bubble attachment difficult and hence reduces the separation efficiency. Several literature results reported that the particle size of the formed CaF_2 precipitate was about 2 μm [10]. However, the turbidity removal efficiency clearly improved with increasing coagulant concentration. The removal efficiency was 97% for a 160 mg/L coagulant dose. Further additive dose did not have a significant effect. The coagulant agents, such as iron and aluminium sulphates have the property to reduce the electrostatic barrier surrounding the colloidal particles. The metal ions cause a coagulation of the colloidal matter, resulting in the formation of rather large particles (flocs), which can be attached to the surface of the gas bubble and be easily entrained towards the surface. Indeed, the increase in the metal sulphate concentration causes the acceleration of the flocculation and the increase of floe sizes [21,23]. Moulai Mostefa and Tir [21] found that the rate of elimination of oil emulsion by EF increases with the concentration of the coagulant agents. The efficiency can reach a value of 99% for concentrations out of Al^{3+} of 200 mg/L. Besides, a

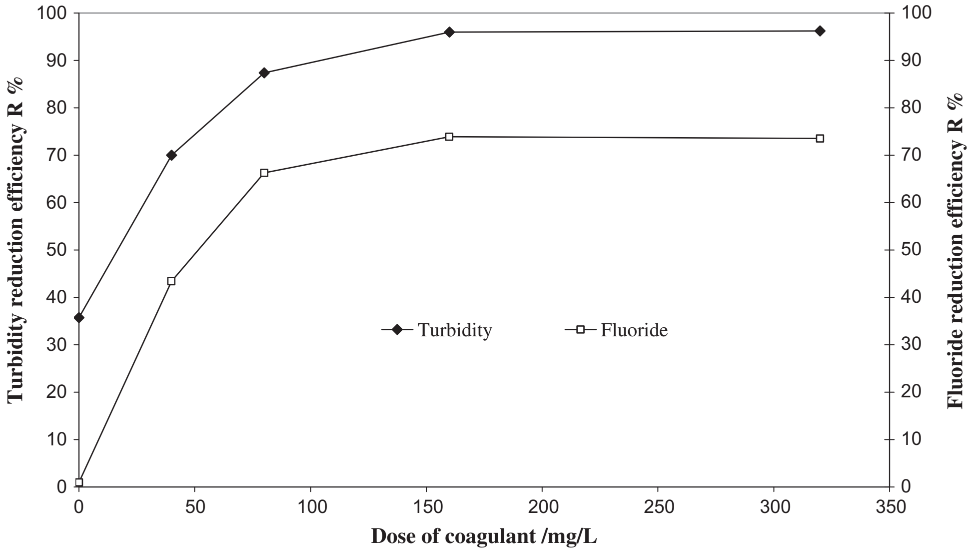

Fig. 2. Effect of coagulant dose on fluoride and turbidity removal, pH 6; $i = 100$ mA, $[F^-]_0 = 38$ mg/L, [Ca]/[F] = 0.5, $t_{EF} = 60$ min.

simultaneous removal of fluoride may be also observed. In fact, an optimum fluoride removal of 73.87% was achieved at 160 mg/L. Recently, Gurtubay et al. [29] studied the treatment of an industrial effluent containing sulphide and fluoride using $Al_2(SO_4)_3$ as coagulant. They found that the fluoride concentration can be reduced from 58 to 5.3 mg/L only on addition of 2,500 mg/L Ca^{2+} and 250 mg/L Al^{3+}.

3.2. Effect of treatment time

In the electrochemical process, the treatment duration is a crucial parameter. The clarification by EF was studied within this duration. The results from Fig. 3 show that turbidity records a sharp decrease in the first moments. After that, it does not change significantly. After 20 min of EF, turbidity passes from 150 to 10 NTU which represents 93% of removal efficiency, while passing from 10 to 4.4 NTU is achieved in 40 min.

3.3. Effect of initial pH

The initial pH is a very important factor that determines the physico-chemical properties of species in the solution. In order to study its effect on treatment efficiency, the following pH values: 4, 5, 6 and 10 were chosen. Fig. 4 indicates that the best results are obtained for initial pH values 5 and 6 with more than 96% removal efficiencies, while in basic media the efficiencies were 88 and 77.8% for pH values 9 and 11, respectively. A weaker value was obtained with acidic pH 4, with 73% removal efficiency. These results are in good agreement with those reported in the literature [24]. It has been established that coagulation efficiency is tightly linked to the presence of the insoluble $Al(OH)_3$ [5–8,12,16] The examination of activity–pH diagram for Al^{+3} species in equilibrium with solid phase $Al(OH)_3$, indicates that the minimum solubility of aluminium hydroxide is recorded at about pH 6. The flocs of $Al(OH)_{3(s)}$ precipitates have large surface areas, which are useful for a rapid adsorption of soluble inorganic compounds and trapping of colloidal particles [24]. At low pH, cationic soluble species Al^{3+} and $Al(OH)^{2+}$ are predominant. When pH is higher than 10, the soluble $Al(OH)_4^-$ anion are the more dominant species.

3.4. Effect of current intensity

Current intensity is the most important electrochemical parameter. In addition to energy consumption, many other properties are related to this parameter. Current intensity directly influences the number and the size of electrogenerated bubbles. In this study, current intensity effect on turbidity removal was studied in the range from 100 to 250 mA. The obtained results are presented in Fig. 5. It may be observed that the optimal value was obtained with 150 mA with 97% removal efficiency. The value 100 mA gives 86% elimination. For weaker values, the process did not take place because of the concomitance of settling which competes with electroflotation.

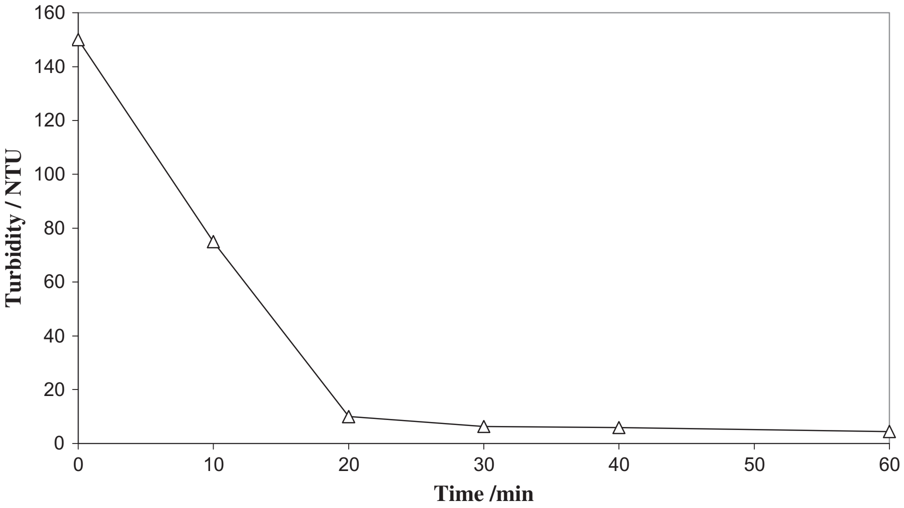

Fig. 3. Effect of treatment time on turbidity removal, pH 6; *i* = 100 mA, $[Al^{3+}]$ = 160 mg/L, [Ca]/[F] = 0.5.

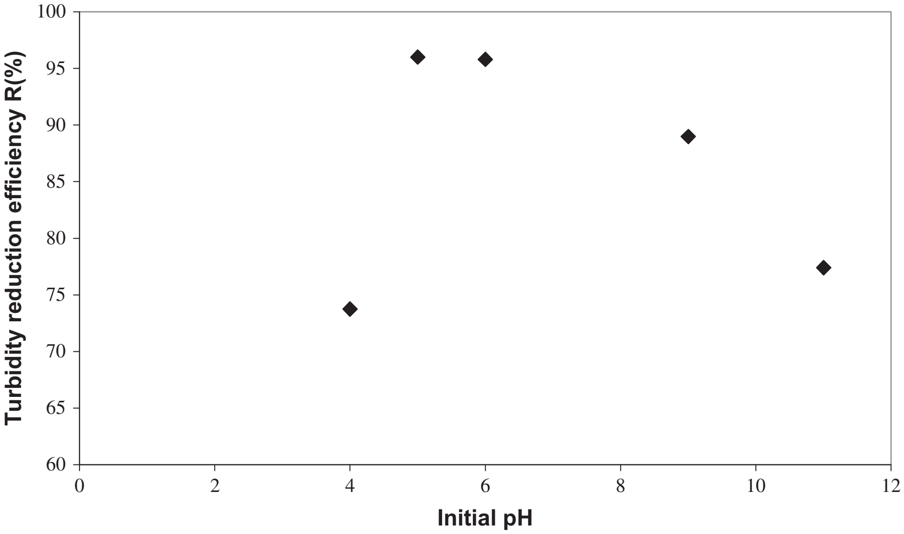

Fig. 4. Effect of initial pH on turbidity reduction, *i* = 100 mA, $[Al^{3+}]$ = 160 mg/L, [Ca]/[F] = 0.5.

For current intensities higher than 150 mA, the efficiency decreased to 78% for 250 mA current intensity. A similar trend was found by Hosny [19] and Ben Mansour and Chalbi [14] when studying oil emulsion removal by EF. According to Hosny [19], the percentage oil removal increases with an increase in current up to an optimum current value. Further increase in the current reduces the removal efficiency. Furthermore, it has been demonstrated by previous studies [18–23] that increasing the current enhances the generation of hydrogen and oxygen gases at the electrode surfaces. This leads to an increase in the number of gas bubbles inside the cell. Consequently, the attachment step between gas bubbles and precipitates is enhanced and more precipitates are carried up by gas bubbles. However, further increase in the current above the optimum value greatly increases the number of gas bubbles generated. There is then a greater possibility that bubbles will coalesce instead of attaching precipitates.

3.5. Effect of neutralizing salt nature

In semiconductor wastewater treatment plants, lime ($Ca(OH)_2$) is currently used in order to reduce fluoride concentration. This is because of its

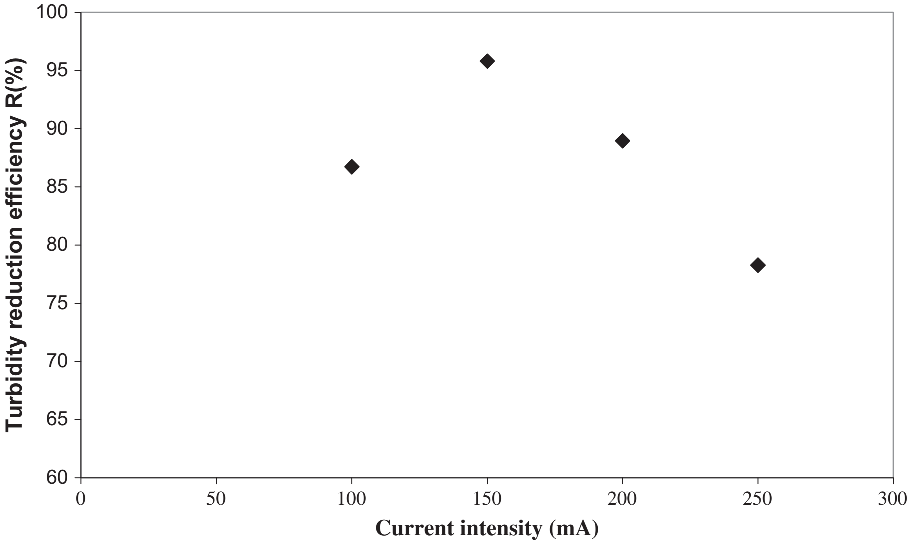

Fig. 5. Effect of current intensity on turbidity reduction, pH 6, $[Al^{3+}]$ = 160 mg/L, [Ca]/[F] = 0.5.

cheapness and its pH neutralizing effect. However, some units use calcium chloride ($CaCl_2$) instead of lime because $CaCl_2$ gives lower final fluoride concentrations. The efficiency of removal of turbidity by EF for both salts was compared. Results from Fig. 6 indicate that with calcium chloride the efficiency was about 67% while it was 97% for lime. This may be explained by the size of CaF_2 particles originating from the reaction of fluoride with $CaCl_2$ which are too fine and hence require higher doses of $Al(OH)_3$ to ensure coagulation [1]. Jadhav et al. [10] stated that the particle size obtained with $Ca(OH)_2$ is greater than that obtained with $CaCl_2$. This is due to the fact that, lime itself acts as a coagulant when dissolved in water. The authors found that the maximum particle size of calcium fluoride (CaF_2) was observed to be around 1 and 0.5 µm for $Ca(OH)_2$ and $CaCl_2$ respectively.

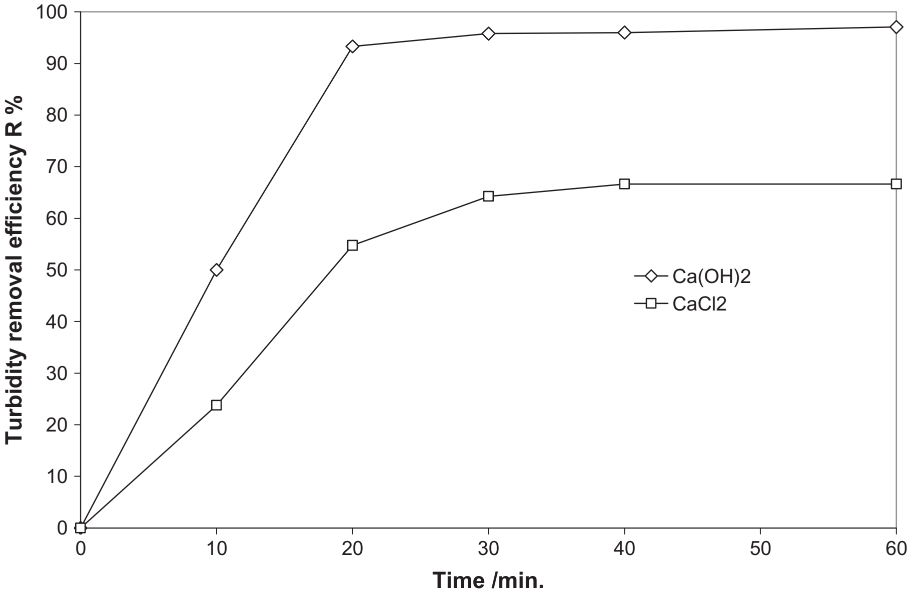

Fig. 6. Effect of neutralizing salt nature on turbidity removal efficiency; pH 6; *i* = 100 mA, $[Al^{3+}]$ = 160 mg/L, [Ca]/[F] = 0.5.

3.6. Energy consumption

Energy consumption EC (kW h/m^3) for the EF process was calculated with the following equation:

$$\mathrm{EC} = \frac{IUt}{v} \tag{5}$$

where U, I and t are respectively the applied voltage (volt), current (ampere) and electrolysis time (hour) and v is the volume in m^3 of the treated solution. Under optimal conditions, the calculated EC was found to be equal to 0.4 kW h/m^3. Ben Mansour and Chalbi [14] found that electrical energy consumption varied from 0.4 to 1.6 kW h/m^3 when studying oil removal by EF, while Bande et al [30] reported that, under optimum conditions, the energy consumption was 0.67 kW h/m^3 for the treatment of oil field effluent by EF.

4. Conclusion

In this study, electroflotation was associated to the existing coagulation technique as an alternative to conventional separation methods. The results show that coagulation–electroflotation technique can be successfully used as an efficient process to treat semiconductor wastewater effluent after the precipitation step and it leads to high clarification efficiency. The obtained results demonstrate the double role of aluminium salts which have a coagulating effect for CaF_2 particles and an adsorbing effect for dissolved fluoride ions. Furthermore, the study demonstrates that the main parameters affecting turbidity removal are coagulant dose, initial pH, time of electrolysis, nature of neutralizing salt and current intensity.

The optimal values are: 160 mg/L coagulant dose, initial pH between 5 and 6, lime as neutralizing salt and current intensity of 150 mA. The obtained removal efficiencies are satisfactory. Under the optimum conditions, the separation of liquid–solid in terms of turbidity reduction was 97% complying with the water reuse standards.

Acknowledgements

This study was financially supported by the National Research Fund from DGRSDT/MESRS (Algeria).

References

[1] C. Huang, J.C. Liu, Precipitate flotation of fluoride-containing wastewater from a semiconductor manufacturer, Water Res. 33 (1999) 3403–3412.
[2] N. Drouiche, S. Aoudj, H. Lounici, M. Drouiche, T. Ouslimane, N. Ghaffour, Fluoride removal from pretreated photovoltaic wastewater by electrocoagulation: an investigation of the effect of operational parameters, Procedia Eng. 33 (2012) 385–391.
[3] N. Parthasarathy, J. Buffle, W. Haerdi, Combined use of calcium salts and polymeric aluminium hydroxide for defluoridation of waste waters, Water Res. 20 (1986) 443–448.
[4] N. Drouiche, S. Aoudj, H. Lounici, H. Mahmoudi, N. Ghaffour, M.F.A. Goosen, Development of an empirical model for fluoride removal from photovoltaic wastewater by electrocoagulation process, Desalin. Water Treat. 29 (2011) 96–102.
[5] S. Aoudj, A. Khelifa, N. Drouiche, M. Hecini, HF wastewater remediation by electrocoagulation process, Desalin. Water Treat. 51 (2013) 1596–1602.
[6] S. Aoudj, N. Drouiche, M. Hecini, T. Ouslimane, B. Palaouane, Coagulation as a post-treatment method for the defluoridation of photovoltaic cell manufacturing wastewater, Proc. Eng. 33 (2012) 111–120
[7] A.H. Essadki, B. Gourich, Ch. Vial, H. Delmas, M. Bennajah, Defluoridation of drinking water by electrocoagulation/electroflotation in a stirred tank reactor with a comparative performance to an external-loop airlift reactor, J. Hazard. Mater. 168 (2009) 1325–1333.
[8] M. Bennajah, B. Gourich, A.H. Essadki, Ch. Vial, H. Delmas, Defluoridation of Morocco drinking water by electrocoagulation/electroflottation in an electrochemical external-loop airlift reactor, Chem. Eng. J. 148 (2009) 122–131.
[9] M. Behloul, H. Grib, N. Drouiche, N. Abdi, H. Lounici, N. Mameri, Removal of malathion pesticide from polluted solutions by electrocoagulation: Modeling of experimental results using response surface methodology, Separ. Sci. Technol. 48 (2013) 664–672.
[10] S.V. Jadhav, C.R. Gadipelly, K.V. Marathe, V.K. Rathod, Treatment of fluoride concentrates from membrane unit using salt solutions, J. Water Process Eng. 2 (2014) 31–36.
[11] R. Aldaco, A. Irabien, P. Luis, Fluidized bed reactor for fluoride removal, Chem. Eng. J. 107 (2005) 113–117.
[12] A.R. Rahmani, Removal of water turbidity by the electrocoagulation method, J. Res. Health Sci. 8 (2008) 18–24.
[13] C.Y. Hu, S.L. Lo, W.H. Kuan, Y.D. Lee, Removal of fluoride from semiconductor wastewater by electrocoagulation–flotation, Water Res. 39 (2005) 895–901.
[14] L. Ben Mansour, S. Chalbi, Removal of oil from oil/water emulsions using electroflotation process, J. Appl. Electrochem. 36 (2006) 577–581.
[15] B.M. Yang, C.J. Huang, W.L. Lai, C.C. Chang, C.M. Kao, Development of a three-stage system for the treatment and reclamation of wastewater containing nano-scale particles, Desalination 284 (2012) 182–190.
[16] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.
[17] A. Khelifa, S. Aoudj, S. Moulay, M. Hecini, M. De Petris-Wery, Degradation of EDTA by in-situ electrogenerated active chlorine in an electroflotation cell, Desalin. Water Treat. 7 (2009) 119–123.
[18] F.N.B. Nahui, M.R. Nascimento, E.B. Cavalcanti, E.O. Vilar, Electroflotation of emulsified oil in industrial wastes evaluated with a full factorial design, Braz. J. Chem. Eng. 25 (2008) 435–442.

[19] A.Y. Hosny, Separation of oil from oil/water emulsions using an electroflotation cell with insoluble electrodes, Filtr. Sep. 29 (1992) 419–423.

[20] P.C.P. Calvin, Electroflotation for groundwater decontamination, J. Hazard. Mater. 55 (1997) 150–170.

[21] N. Moulai Mostefa, M. Tir, Coupling flocculation with electroflotation for waste oil/water emulsion treatment. Optimization of the operating conditions, Desalination 161 (2004) 115–121.

[22] L. Ben Mansour, I. Kesentini, Treatment of effluents from cardboard industry by coagulation–electroflotation, J. Hazard. Mater. 153 (2008) 1067–1070.

[23] L. Ben Mansour, I. Ksentini, B. Elleuch, Treatment of wastewaters of paper industry by coagulation–electroflotation, Desalination 208 (2007) 34–41.

[24] A.Z. Bouyakoub, S. Kacha1, R. Ouhib, S. Bellebia, B. Lartiges, Combined treatment of a textile effluent containing reactive dyes by coagulation–flocculation and electroflotation, Rev. Sc. Eau. 23 (2010) 89–103.

[25] X. Chen, G. Chen, Stable Ti/RuO_2–Sb_2O_5–SnO_2 electrodes for O_2 evolution, Electrochim. Acta 50 (2005) 4155–4159.

[26] V.A. Kolesnikov, S.O. Varaksin, L.A. Kryuchkova, Electroflotation extraction of valuable components from wash waters of electroplating works with water recycling, Russ. J. Electrochem. 37 (2001) 760–764.

[27] A. Khelifa, S. Aoudj, S. Moulay, M. De Petris-Wery, A one-step electrochlorination-electroflotation process for the treatment of heavy metals wastewater in presence of EDTA, Chem. Eng. Process 70 (2013) 110–116.

[28] A.E. Greenberg, L.S. Clesceri, A.D. Eaton, Standard Methods: For the Examination of Water and Wastewater, 18th ed., APHA, Washington, DC, 1992.

[29] L. Gurtubay, I. Dañobeitia, A. Barona, J. Prado, A. Elías, Viability study on two treatments for an industrial effluent containing sulphide and fluoride, Chem. Eng. J. 162 (2010) 91–96.

[30] R.M. Bande, B. Prasad, I.M. Mishra, K.L. Wasewar, Oil field effluent water treatment for safe disposal by electroflotation, Chem. Eng. J. 137 (2008) 503–509.