



## Original Article

# Study of electroflotation method for treatment of wastewater from washing soil contaminated by heavy metals

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### ABSTRACT

Electroflotation method (EFM) for treatment of synthetic solutions simulating wastewater from washing soil contaminated by drilling fluids from oil wells was investigated in this paper. Experiments were carried out to examine the effects of the operating conditions on the removal of lead, barium and zinc from solutions containing  $15 \text{ mg dm}^{-3}$  for each metal representing a typical concentration of wastewater generated in the washing soil in this treatment. The experimental results showed that it is possible to remove these heavy metals by electrocoagulation/electroflotation (ECF) attaining 97% of removal using stainless steel mesh electrodes with a power consumption of  $14 \text{ kWh m}^{-3}$ . The optimal conditions of treatment were sodium dodecyl sulfate (SDS) in a molar ratio 3:1, current density around  $350 \text{ A m}^{-2}$ , ionic strength  $3.2 \times 10^{-3} \text{ M}$ ,  $\text{pH} = 10.0$  and 20 min of ECF. This study newly indicated that the proposed method is adequate to simultaneously treat the common heavy metals found in the drilling fluids oil wells.

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## 1. Introduction

Environmental pollution caused by heavy metals from different economic activities constitutes a serious risk for the environment. The oil wells drilling have been one source of soil contamination by lead (Pb), barium (Ba) and zinc (Zn), due to the composition that contains substances such as barite and galena, which are used for density control of drilling fluids.

The soil washing is a technique that separates a variety of inorganic contaminants of the clay fraction. When this remediation technique was used in contaminated soil samples from the region of Mato Rico and Santa Maria do Oeste (Paraná, Brazil), it generated a large amount of diluted wastewater whose initial concentrations of Pb, Ba and Zn ions were around  $15 \text{ mg dm}^{-3}$  for each heavy metal. Due to their high solubility in the aquatic environments, the heavy metals, known as powerful toxic agents, can be absorbed by living organisms and may accumulate in the human body [1–4].

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The traditional techniques for wastewater treatment do not show satisfactory performance for very dilute solutions (concentration below  $50 \text{ mg dm}^{-3}$ ), mainly due to the low operational efficiency and high extraction costs [2,3]. In this way, an alternative method, such as the electroflotation (EFM), has been proposed as an efficient alternative treatment method that can be applied for small, medium or even large scales [5-14]. The EFM is a simple process that floats ions or solid particles, suspended or dissolved in a liquid phase, by the adhesion on tiny bubbles of hydrogen and oxygen formed on cathode and anode and moves upward in the flotation cell. The key to floatability of chemical species is the hydrophobicity, the ratio of collector to metal ion being an important factor; hence, the amount of collector used in ion flotation should be at least stoichiometric with foamy properties [7].

The electrode selection allows configuring the system for a specific process: soluble anodes, as made by iron or aluminum, generate coagulants agents *in situ* promoting the simultaneous electrocoagulation (EC) phenomenon. It is generally accepted that the EC process involves three stages. The first stage consists of electrode oxidation to form coagulants agents. Simultaneously, the water electrolysis occurs. At stainless steel electrodes, the following reactions take place [14,15]:

Anode:



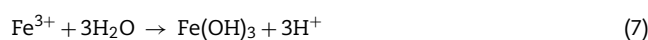
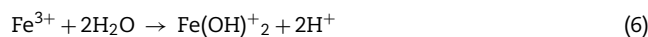
Cathode:



In practice, the second anode reaction (Eq. (2)) must be dominant and bubbles of gas are observed at both electrodes. The second stage of EC involves destabilization. An electrochemical reduction of metal cations may occur on cathode surface and the hydroxide ions formed at the cathode increase the pH of the wastewater thereby inducing precipitation of metal ions.



However,  $\text{Fe}^{3+}$  ions can be formed at acidic pH and in the presence of oxygen. Depending on pH, the species  $\text{Fe}(\text{OH})^{2+}$ ,  $\text{Fe}(\text{OH})^+$  and  $\text{Fe}(\text{OH})_3$  may be present in the solution.



Under alkaline conditions,  $\text{Fe}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_4^-$  are present in more quantity in solution and it can be expected to occur also in absorption and adsorption of heavy metals by these compounds. So, the last EC stage consists of aggregation of the destabilized phases to form flakes [16,17].

The objective of this work is to remove Pb, Ba and Zn ions of solutions that simulates wastewater from washing soil

contaminated by drilling fluids from oil wells by ECF using stainless steel mesh electrodes. Parameters such as current density, ionic strength, pH and time of EF were investigated to enhance the efficiency of treatment. This paper proposes an electroflotation method that simultaneously removes the Pb, Ba and Zn in solutions with low concentrations compatible with those obtained in the washing steps of the contaminated soil treatment during the drilling wells of oil production [18,19].

## 2. Methods

The flotation cell used in this study was designed with  $13 \text{ cm} \times 13 \text{ cm} \times 13 \text{ cm}$  acrylic cube and peripherals. Fig. 1 shows the experimental apparatus composed by a continuous current (CC) supply 0-30 V/0-15 A connected to the soluble electrodes through an isolated copper wire. The electrodes which correspond to  $S = 40 \text{ cm}^2$  were assembled with a stainless steel wire (0.4 mm diameter) disposed on handmade acrylic frame, located on the flotation cell bottom. The distance between both electrodes was  $e = 10 \text{ mm}$ .

All the runs were carried out at a room temperature ( $28^\circ \text{C}$ ). In each run,  $1 \text{ dm}^3$  of stocked synthetic wastewater was added to the flotation cell. The collector (SDS) was added in the correct ratio as well as the pH regulators and bubbly agent (ethanol). The CC font was turned on and the procedure was initiated. After flotation time (specific for each test) the samples were collected and taken to atomic absorption analysis. It is important to report that the initial pH varies along the experiments, being necessary small adjustments to keep the desired during the experiments.

All experiments were carried out on bench scale and the chemicals used were listed as follows: lead II sulfate ( $\text{PbSO}_4$ , VETEC, Brazil), barium sulfate ( $\text{BaSO}_4$ , ISOFAR, Brazil), zinc sulfate anhydrous ( $\text{ZnSO}_4$ , VETEC, Brazil), sodium sulfate ( $\text{Na}_2\text{SO}_4$ , VETEC, Brazil), sodium dodecil sulfate ( $\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$ , B'HERZOG, Brazil), sulfuric acid ( $\text{H}_2\text{SO}_4$ , VETEC, Brazil), sodium hydroxide ( $\text{NaOH}$ , VETEC, Brazil), ethyl alcohol ( $\text{C}_2\text{H}_6\text{O}$ , B'HERZOG, Brazil) and distilled water. All chemicals were of analytical grade.

The sampling method was carried out for different time intervals, current densities and concentrations, depending on the runs. The samples were collected within the solution suitable for atomic absorption analysis technique. The foam was not analyzed.

## 3. Results and discussions

EF is reported to be strongly dependent on pH. This trend is confirmed by Fig. 2 that shows the effect of the pH on the Pb removal. In fact, when the pH varies, heavy metals species take different reactivity. The efficiency of the removal of heavy metal during the treatment was evaluated by its removal efficiency ( $\eta$ ) given by Eq. (8) [15-26]:

$$\eta(\%) = \frac{c_0 - c}{c_0} \times 100 \quad (8)$$

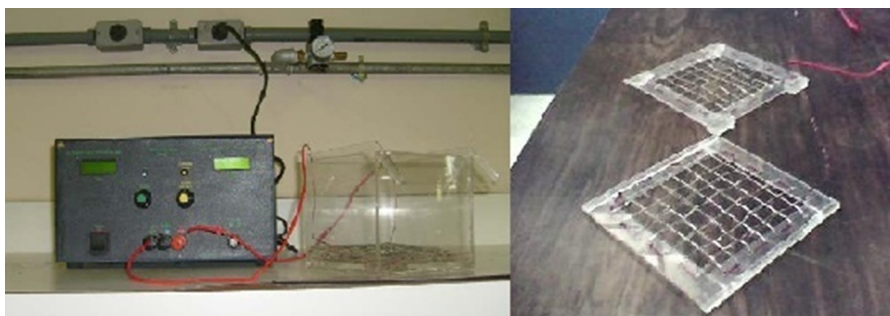


Fig. 1 – Experimental EF unit and stainless steel mesh electrodes.

where  $C_0$  and  $C$  are, respectively, the concentrations ions before and after the treatment.

The  $Pb^{2+}$  speciation diagram (Fig. 2) was constructed using the MEDUSA software [24]. This diagram indicates the predominance of  $Pb^{2+}$  specie in the pH <6.0 range which allows the use of an anionic collector; therefore, SDS collector was chosen. Fig. 2 also shows the formation of the anionic species complex in very basic pH (above 12). Consequently, as SDS is an anionic collector, the floatability above pH 10.0 was not studied which is corroborated with previous literature data [27].

In EF tests, stainless steel mesh electrodes were used, and EF involved in situ generation of coagulant. The iron ions generation in solution occurs initially with  $Fe^{+2}$ . In alkaline conditions,  $Fe^{+2}$  species can hydrolyze and in acid conditions  $Fe^{+3}$  ions may be formed. Therefore, the study of the pH effect on Pb removal initially on pH = 4.0 was investigated, as shown in Fig. 3.

Fig. 3, as expected, shows that the electrolytic process is also influenced by time. After 5 min it was possible to obtain above 94% removal of Pb. The EF kinetics is strongly influenced by the amount of bubbles dispersed within the solution. Since the tests were conducted under the same current density and the same ionic strength, the amount of bubbles remained theoretically constant during the runs. In spite of high process efficiency under all conditions examined, from the environmental standpoint, 20 min were enough to attain the concentration, according to Brazilian environmental laws, that stands the maximum concentrations of Pb, Zn and Ba for effluent discharge are  $0.5\text{ mg dm}^{-3}$ ,  $5.0\text{ mg dm}^{-3}$  and  $5.0\text{ mg dm}^{-3}$ , respectively. In the literature, the study of individual heavy metal ions is well established [3–5]. However,

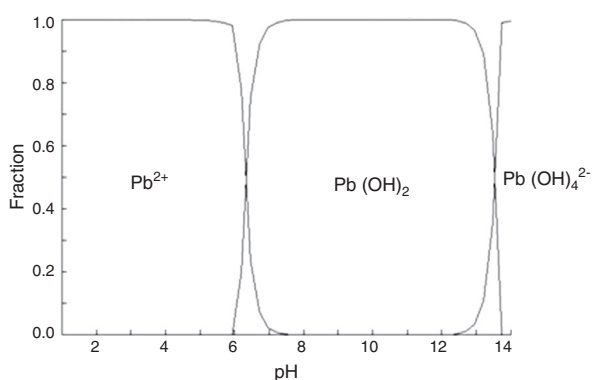


Fig. 2 –  $Pb^{2+}$  species fraction diagram ( $[Pb^{2+}] = 15\text{ mg dm}^{-3}$ ).

the removal efficiency of heavy metal ions in wastewater containing several ions usually presents quite different trends [22–30]. In this sense, this paper presents novelty. For the Pb, Ba and Zn ions simultaneously the final efficiency is higher compared with other methods and lower when compared with individual ions, depending on the characteristics of coagulation and charge interactions [22–26].

Previous works on ion flotation have indicated that the use of specific stoichiometric ratios of collectors plays an important role in the removal performance [11]. The heavy metal/collector ratio has not been the object of this work, the selected ratio was based on the work of Martins et al. [21], which concluded that the highest removal efficiency of Pb by dissolved air flotation can be obtained using 1:3 metal/collector (SDS) ratio, for the same initial concentration of  $Pb:15\text{ mg dm}^{-3}$ , which is justified by the similarities of the experiments. Similar results can be found elsewhere [26–30]. When collector/heavy metal ratio is low, a very thin and unstable foam layer was formed at the top of the cell [1]. As shown in Fig. 3, theoretically the pH = 8.0 is the best point for the Pb ECF during the first 20 min of flotation. Similar pH condition was indicated by Martins et al. [21] and depending on the ions interactions the recommended electroflotation time may change [18–26].

Fig. 4 shows the effect of the current density on Pb removal by ECF. Although almost constant, an average removal of 92% was achieved. Comparing the results obtained in this study with similar ones described by other authors [22,25–28], it can be observed that the current density did not prove to give

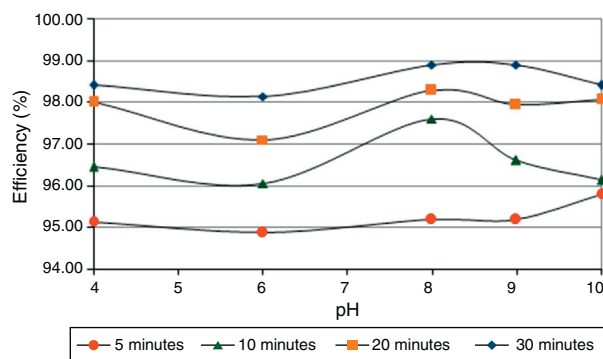
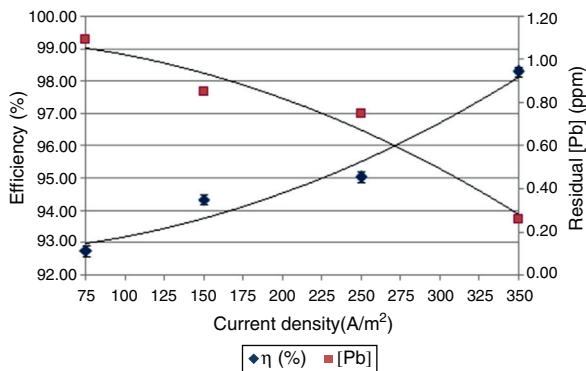


Fig. 3 – Removal of Pb as a function of the pH and the time (Pb:SDS ratio = 3, ionic strength  $3.2 \times 10^{-3}\text{ M}$ , 0.1%, v/v ethanol and  $350\text{ A m}^{-2}$ ).



**Fig. 4 – Removal of Pb as a function of the current density (Pb:SDS ratio = 3, pH = 8.0, 20 min of EF, 0.1%, v/v ethanol and ionic strength  $3.2 \times 10^{-3}$  M).**

meaningful results in the studied range. The electrochemical reaction was found to be limited, probably due to diffusion, resulting in a linear relationship between the current density and the Pb removal, as shown in Fig. 5. The increase of tension promoted an increase in bubbles swarm, nevertheless insufficient to increase the Pb removal.

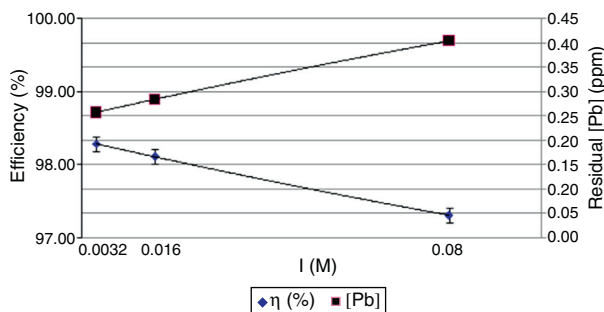
The ionic strength (*I*) is a measure of the electrical potential of the solution. Generally, in ECF process, the increase in ionic strength causes an expansion in conductivity, and this usually leads to a gain in removal efficiency [26,30]. The ionic strength is defined by Eq. (9):

$$I = \frac{1}{2} \sum_i C_i z_i^2 \tag{9}$$

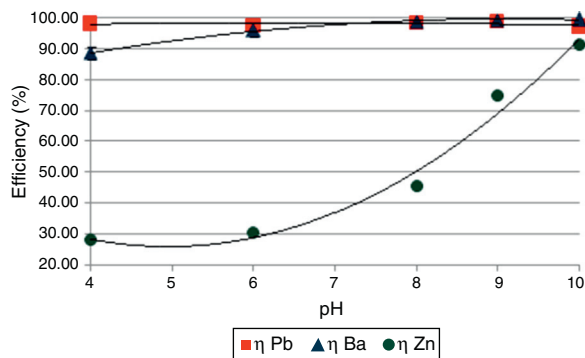
where *C<sub>i</sub>* is the molal concentration of each ion, for dilute solutions it is possible to use the molar concentration as a good approximation, and *z<sub>i</sub>* is the charge on each ion in solution.

The experimental results of the effect of added supporting electrolyte on Pb removal are shown in Fig. 5 where the ionic strength was agreed with sodium sulfate. There has been a slight decrease in removal efficiency with increasing ionic strength of the system. This can be explained, probably, by the competition of ions with other ions to adhere with the collector. This trend is confirmed by previous work concerned with water treatment [5,7,25].

The tests for Pb removal by ECF showed that there are certain conditions where the ECF technique was able to produce



**Fig. 5 – Removal of Pb as a function of the ionic strength (Pb:SDS ratio = 3, pH = 8.0, 0.1%, v/v ethanol, 20 min of EF and  $350 \text{ A m}^{-2}$ ).**



**Fig. 6 – Removal of Pb, Ba and Zn as a function of the pH (Heavy metal:SDS ratio = 3, ionic strength  $3.2 \times 10^{-3}$  M, 20 min of EF and  $350 \text{ A m}^{-2}$ ).**

results in agreement with Brazilian standard emission limits. The optimum conditions for removing Pb from a solution with  $15 \text{ mg dm}^{-3}$  as an initial concentration is current density of  $350 \text{ A m}^{-2}$ ,  $3.2 \times 10^{-3}$  M of ionic strength, 20 min of flotation time, Pb:SDS ratio = 3 and pH = 8.0.

Using the above optimal conditions found in the Pb ECF, with the exception of pH, which was evaluated again, the ECF technology was studied on Pb, Ba and Zn removal from a synthetic effluent simulating wastewater from washing soil contaminated by drilling fluids. Initial concentrations of Pb, Ba and Zn equal to  $15 \text{ mg dm}^{-3}$  for each heavy metal were employed, close to the true effluent concentrations obtained by soil washing. The results are shown in Fig. 6. The pH = 10.0 is suggested as the best pH for the simultaneous removal of metals under operating conditions studied.

Under the experimental conditions studied, it has been found that the voltage increased linearly with the current applied on electrodes. One of the most important parameters, that affect the application of ECF technique for wastewater treatment, was the power consumption. The energy (*E*) consumed during the electrolytic process ( $\text{kWh m}^{-3}$ ) could be calculated by Eq. (10) [27]:

$$E = \frac{Uit}{1000V} \tag{10}$$

where *U* is the applied voltage (V), *i* is the current (A), *t* is the time flotation (hour) and *V* is the volume of the effluent treated ( $\text{m}^3$ ).

The specific power consumption achieved in this ECF process was calculated as  $14 \text{ kWh m}^{-3}$ , which represents a relative low cost of the treatment when compared with other methods [2-6].

#### 4. Conclusions

The performance of batch ECF technique for the treatment of synthetic solutions simulating wastewater from washing soil contaminated by drilling fluids from oil wells was investigated. The effects of different parameters, including the pH, the electrolysis time, the current density and the supporting electrolyte dosage were evaluated. Some parameters as pH



and ECF time investigated were very important for design optimal conditions of the treatment. However, some variables tested, such as ionic strength and current density, were not proved to be very important under the conditions studied.

The experimental results revealed that it was feasible to remove up to 97% of the Pb, Ba and Zn by ECF method with a total energy consumption of 14 kWh m<sup>-3</sup>. The optimum conditions found in this work were as follows: current density 350 A m<sup>-2</sup>, ionic strength 3.2 × 10<sup>-3</sup> M, pH = 10.0 and 20 min of ECF, 0.1% ethanol (as a foamy) and molar ratio 3:1 SDS:heavy metal. The investigation of an efficient new method to treat effluents which contains simultaneously Pb, Ba and Zn is proposed. The overall removal to attain the Brazilian laws was compatible with operation time feasible in the industrial scale with relative low cost. This technique is expected to be also efficient for other effluents which contain other heavy metals with small adjustments on the operating conditions.

### Conflicts of interest

The authors declare no conflicts of interest.

### Acknowledgments

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### REFERENCES

- Zouboulis AI, Goetz L. Ion flotation as a tool for speciation studies selective separation in the system Cr<sup>3+</sup>/Cr<sup>6+</sup>. *Toxicol Environ Chem* 1991;31-32:539–47.
- Kuokkanen V, Kuokkanen T, Ramo J, Lassi U. Recent applications of electrocoagulation in treatment of water and wastewater – a review. *Green Sustain Chem* 2013;3: 89–121.
- Chopra AK, Sharma AK, Kumar V. Overview of electrolytic treatment: an alternative technology for purification of wastewater. *Arch Appl Sci Res* 2011;3:191–206.
- Butler E, Hung YT, Yeh RYL, Al Ahmad MS. Electrocoagulation in wastewater treatment. *Water* 2011;3: 495–525.
- Kurniawan TA, Chan GYS, Lo WH, Babel S. Physico-chemical treatment techniques of wastewater laden with heavy metals. *Chem Eng J* 2006;118:83–98.
- Baghban E, Mehrabani-Zeinabad A, Mohed A. The effects of operational parameters on the electrochemical removal of cadmium ion from dilute aqueous solutions. *Hydrometallurgy* 2014;149:97–105.
- Nanseu-Njiki CP, Tchamango SR, Ngom PC, Darchen A, Ngameni E. Mercury(II) removal from water by electrocoagulation using aluminium and iron electrodes. *J Hazard Mater* 2009;168:1430–6.
- Choi J, Shim S, Yoon J. Design and operating parameters affecting an electrochlorination system. *J Ind Eng Chem* 2013;19:215–9.
- Mouli PC, Mohan SV, Reddy SJ. Electrochemical processes for the remediation of wastewater and contaminated soil: emerging technology. *J Sci Ind Res* 2004;63:11–9.
- Nerbittand CC, Davis TE. Removal of heavy metals from metallurgical effluents by the simultaneous precipitation and flotation of metal sulfides using column cells, extraction and processing for the treatment and minimization of wastes. *Miner Met Mater Soc* 1994:331–42.
- Casqueira RG, Torem ML, Koler HM. The removal of zinc from liquid streams by electroflotation. *Miner Eng* 2006;19:1388–92.
- Shakir IK, Hussein BI. Lead removal from industrial wastewater by electrocoagulation process. *Iraqi J Chem Petrol Eng* 2009;10:35–42.
- Mollah MYA, Schennach R, Parga JR, Cocke DL. Electrocoagulation (EC) – science and applications. *J Hazard Mater* 2001;84:29–41.
- Matis KA, Mavros P. Recovery of metals by ion flotation from dilute aqueous solutions. *Sep Purif Methods* 1991;20:1–48.
- Mohammadand ME, Muttucumar S. Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes. *J Environ Manage* 2009;90:1663–79.
- Aji BA, Yavuz Y, Koparal AS. Electrocoagulation of heavy metals containing model wastewater using monopolar iron electrodes. *Sep Purif Technol* 2012;86:248–54.
- Parga JR, Cocke DL, Mencer DE, Morkovsky P. Electrocoagulation of heavy metals and characterization of the process. In: *Proceedings of the TMS fall 2002 extraction and processing division meeting*, vol. 1. 2002. p. 671–80.
- Hosny AY. Separating oil from oil–water emulsions by electroflotation technique. *Sep Technol* 1996;6:9–17.
- Bande RM, Prasad B, Mishra IM, Wasewar KL. Oil field effluent treatment waste treatment for safe disposal by electroflotation. *Chem Eng J* 2008;137:505–509.
- Xu D, Tan X, Chen X, Wang X. Removal of Pb(II) from aqueous solution by oxidized multiwalled carbon nanotubes. *J Hazard Mater* 2008;154:407–16.
- Martins ALS [M.Sc. dissertation] Removal of lead and barium from a wastewater by dissolved air flotation. Brazil: Federal Rural University of Rio de Janeiro; 2009.
- Burns SE, Yiacoumi S, Tsouris C. Microbubble generation for environmental and industrial separations. *Sep Purif Technol* 1997;11:221–32.
- Unran UT, Koparal AS, Ogutveren UB. Fluoride removal from water and wastewater with a batch cylindrical electrode using electrocoagulation. *Chem Eng J* 2013;223: 110–5.
- Puigdomenech I. MEDUSA chemical equilibrium database and plotting software. KTH Royal Institute of Technology; 2004.
- Chen G. Electrochemical technologies in wastewater treatment. *Sep Purif Technol* 2003;28:1–31.
- Khelifa A, Moulay S, Naceur AW. Treatment of metal finishing effluents by the electroflotation technique. *Desalination* 2005;181:27–33.
- Heidmann I, Calmano W. Removal of Ni, Cu and Cr from a galvanic wastewater in an electrocoagulation system with Fe- and Al-electrodes. *Sep Purif Technol* 2010;71:308–14.
- Monsour LB, Ksentini I, Elleuch B. Treatment of wastewaters of paper industry by coagulation-electroflotations. *Desalination* 2007;208:34–41.
- Merzouk B, Madani K, Sekki A. Using electrocoagulation–electroflotation technology to treat synthetic solution and textile wastewater, two case studies. *Desalination* 2010;250:573–7.
- Khelifa A, Aoudj S, Moulay S, de Petris-Wery M. A one-step electrochlorination/electroflotation process for the treatment of heavy metals wastewater in presence of EDTA. *Chem Eng Process Process Intensif* 2013;70:110–6.