Development of a novel electrochemical coagulant dosing unit for water treatment

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Abstract

BACKGROUND

The design of new approaches that help to decrease both the environmental impact of industrial activities and the cost of existing water treatment technologies is becoming a key aspect of research. In the present work, an efficient and easy-to-use electrochemical device designed to dose iron coagulants is presented.

RESULTS

The proposed device (named as Electrochemically-Assisted Coagulant - Production & Dosing Unit, ECU) exhibits an efficient performance in the dosing of coagulants regardless of the ionic conductivity of the water matrixes tested (within the range $100 \mu\text{S cm}^{-1}$ to $1000 \mu\text{S cm}^{-1}$), covering a wide range of potential real surface waters. The behaviour of the ECU device was compared to that of a conventional chemical dosing of iron, showing a better pH (pH around 8 for ECU but lower than 4 for equivalent chemical dosing) and conductivity (decrease for ECU but increase up to 60% for equivalent chemical dosing) control. Moreover, the ECU unit produced a noticeable amount of Fe^{2+} ions, due to the limited access of atmospheric oxygen inside the device.

CONCLUSION

The device developed overcomes traditional chemical iron dosing and could be potentially applied in uses different from electrocoagulation, as it is the case of Fenton related technologies.

Keywords: coagulant dosing; water treatment; electrocoagulation; cell design

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1. Introduction

Electrocoagulation is an electrochemical technology that is currently gaining scientific and industrial interest due to the wide range of applications in which this process has been proven efficient. Thus, electrocoagulation has been successfully applied in the treatment of drinking water ¹⁻⁴, different types of industrial wastewater ⁵⁻⁹, urban wastewater ¹⁰⁻¹² and reclaimed wastewater ¹³⁻¹⁵.

Electrocoagulation is reported to exhibit clear advantages vs. conventional chemical coagulation ^{16, 17}, specifically lower chemical dosing requirements, limited increase (or even decrease) in the ionic conductivity ¹⁸, better pH control ¹⁹ and lower operational cost ²⁰. In addition, this process is known to activate other additional treatment mechanisms such as the electro-flocculation ^{14, 21}, the electro-flotation ^{22, 23} or even the electrochemical disinfection ²⁴.

Nevertheless, some aspects hinder the massive application of electrocoagulation in the industrial environment. As it has been pointed out in a recent review ²⁵, one of the challenges that electrocoagulation technologies should overcome is that the vast majority of the works regarding this technology are focused on the removal of specific pollutants and not on the development and design of new reactor approaches. Moreover, it is affirmed that the future of this technology would depend on the ability of designing reactors that can fulfill commercial criteria, minimizing operational and maintenance costs.

Currently, our research group collaborates in the design of a cost-effective and easy-to-use solution for providing disinfection technologies in rural zones of Africa, in the framework of the H2020 project *SafeWaterAfrica*. In this project, the pre-treatment prior to disinfection is a key aspect because of the occurrence of supply sites with high fecal pollution, caused mainly by farms and/or by urban wastewater discharges. In this context,

coagulation (either chemical or electrochemical) has been proposed as a suitable technology for the treatment of surface water sources and the production & dosing unit proposed here can be a very interesting tool to attain it at low cost and high efficiency, by using the same equipment of conventional coagulation and simply replacing the coagulant preparation and storage facilities and the pumps typically used to dose this chemical reagent by this novel system. Hence, this work presents a novel Electrochemically-assisted Coagulant - production & dosing Unit (ECU) to be used as a low-cost and easy-to-use electrochemical device to provide the required dosing of coagulants in water treatment, to replace the conventional chemical dosing of coagulants. The ECU device was designed to provide a long-time operation and an easy system for replacing the iron bed that is being dissolved, trying to reduce the operating costs and to enhance the real applicability of the device. Regarding the performance of the cell, it aims to exhibit an efficient dosing of iron even with low conductivity water ($100 \mu\text{S cm}^{-1}$). The performance of this unit is going to be compared to that of chemical dosing of iron, in particular with respect to the pH control, changes in the ionic conductivity and ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the coagulant produced.

2. Material and methods.

2.1. Electrochemically-assisted Coagulant-production&dosing Unit (ECU).

Figure 1 shows a picture and a schematic plot of the cell designed for the improved production and dosing of coagulant. It consists in an internal bed of *ca.* 1 kg of iron particles (3) placed inside an internal plastic mesh (4) that allows the pass of the fluid but avoids short-circuit of anode and cathode. The reactor has an internal stainless steel rod (2) immersed inside the bed of iron particles. This internal rod behaves as anode feeder, allowing the anodic dissolution of the iron bed. The cathode is an external stainless steel

tube (1), electrically isolated from the anode by the internal plastic mesh. The cell behaves as a flow-through reactor, in which the fluid enters through the bottom (5) and exits the cell through an overflow (6) at the top. The top of the cell can be easily separated from the body of the cell by a threaded joint in order to allow an easy replacement of the iron bed once it has been completely dissolved.

Fig. 1. Photograph and schematic plot of the ECU. 1: external stainless steel cathode; 2: stainless steel anode feeder; 3) internal bed of iron particles; 4) internal plastic mesh; 5) reactor inlet; 6) reactor outlet

2.2. Experimental procedure.

The experiments were carried out in continuous mode and under galvanostatic conditions. They were performed with a fixed flow rate of 15 L h^{-1} of water across the cell. Each experiment spends 45 min. The current was progressively increased from 0.00 to 0.40 A in steps of 0.10 A, giving results for four increasing values of applied electric charge (ratio of intensity and flow rate). In order to achieve the stabilization of the system, the

samples were taken 5 minutes after the each intensity variation. For the polarization curves, the value of voltage required to obtain the required intensity was registered.

This procedure was repeated for four different matrixes of increasing conductivity: *i*) mixture of tap water and deionized water to give a final conductivity of $100 \mu\text{S cm}^{-1}$; *ii*) tap water (conductivity of $400 \mu\text{S cm}^{-1}$); *iii*) synthetic solution of NaCl with a final conductivity of $1000 \mu\text{S cm}^{-1}$ (0.514 g L^{-1} ; ionic strength of $8.8 \cdot 10^{-3} \text{ mol kg}^{-1}$) *iv*) synthetic solution of Na_2SO_4 with a final conductivity of $1000 \mu\text{S cm}^{-1}$ (0.624 g L^{-1} ; $1.3 \cdot 10^{-2} \text{ mol kg}^{-1}$ of ionic strength). With these four matrixes, we planned to cover different type of potential surface waters of different conductivity and chemical composition. The performance of the ECU device was compared to that of a conventional chemical iron dosing (in the form of FeCl_3). To simulate a real treatment process, the pH of the samples were corrected to 8.0 by adding NaOH. FeCl_3 was purchased from Merck and the rest of reagents (NaCl, Na_2SO_4 and NaOH) were acquired from Panreac (Barcelona, Spain).

Each sample was characterized by physicochemical parameters such as pH, conductivity, Redox potential and iron concentration. Measurements of pH and conductivity were carried out using a CRISON pH25+ and CRISON CM35+, respectively. The redox Potential was measured with a waterproof tester ORP HI 73120 electrode provided by HANNA instruments. Total iron concentration was measured off-line using an inductively coupled plasma spectrometer (Liberty Sequential, Varian).

3. Results and discussion.

Figure 2 shows the polarization curves of the ECU cell obtained for the four water matrixes with different conductivities used as models in this work: $100 \mu\text{S cm}^{-1}$ mixture

of tap and milliQ water, tap water (aprox. $400 \mu\text{S cm}^{-1}$), NaCl solution ($1000 \mu\text{S cm}^{-1}$) and Na_2SO_4 solution ($1000 \mu\text{S cm}^{-1}$).

Fig. 2. Polarization curve for electrochemical coagulant dosing unit (ECU) • $100 \mu\text{S cm}^{-1}$
¹; ▲ tap water; ♦ $1000 \mu\text{S cm}^{-1} \text{SO}_4^{2-}$; ■ $1000 \mu\text{S cm}^{-1} \text{Cl}^-$.

The almost linear relation of intensity vs voltage indicates that this process works in the region of ohmic polarization within the range of conductivities tested in the present work. As expected, the slope of the plot increases for higher ionic conductivities, as the resistance of the electrolyte decreases²⁶⁻²⁹. Hence, for the same cell voltage applied, higher currents can be obtained and hence higher amounts of coagulants are expected to be produced. Unexpectedly, sulfate solution leads to better performance than chloride and this has to be explained in terms of the complex chemistry of chloride anions and the slightly higher ionic strength of the solution of sodium sulfate.

Interestingly, one of the key aspects of the cell is its ability to dissolve the required iron concentration. Thus, Figure 3 represents the iron produced in these tests, together with

the iron dosing predicted by Faraday's Law, considering oxidation of metal iron to Fe^{2+}

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Fig. 3. Fe concentration at the outlet of the electrochemical coagulant dosing unit (ECU)
• 100 $\mu\text{S cm}^{-1}$; ▲ tap water; ♦ 1000 $\mu\text{S cm}^{-1}$ SO_4^{2-} ; ■ 1000 $\mu\text{S cm}^{-1}$ Cl^- ; dashed line: Fe predicted by Faraday's Law.

As observed, the amounts of iron produced are under the expected values, pointing out the occurrence of parasitic reactions, specifically the well-known oxygen evolution ^{17, 21}. The exception to this general behavior is the concentration of iron dissolved (1.3 mg dm^{-3}) when no current is passed through the system. As an aerated solution is passed through the cell, some oxidation of iron by the dissolved oxygen is expected in this system (Equation 1), explaining the slight concentration of iron that was found for null applied electric charge. This behavior has been previously described not only for iron but also for aluminum electrocoagulation ³².

Moreover, it can be observed that the highest efficiency in the dissolution of iron was found for the lowest conductivity solution ($100 \mu\text{S cm}^{-1}$), meanwhile the ECU device exhibits a more similar efficiency with the rest of test waters, just with a slightly lower efficiency in the case of tap water. The higher efficiency for the lowest ionic strength can be attributed to the larger voltage required to work at the same intensity and, as a consequence, at the same applied electric charge according to the data presented and discussed in Figure 2. Moreover, as it will be explained later on the lower ionic strength of this water produce a larger change in the pH and conductivity which can help to explain this higher efficiency in the production of iron coagulants. In addition, the more complex composition of the tap water (in particular with the presence of bicarbonates) can help to explain slightly lower production of iron in that case, due to the lower aggressiveness related to the reduced change in pH and conductivity²⁵. Nevertheless, it is worth mentioning that iron can be dosed to the solution even at very low conductivity, demonstrating the applicability of the device to be used in a wide range of different water matrixes.

Regarding the comparative behaviour of the system with chloride and sulphate as supporting anions, negligible differences were found according to the data included in Figure 3. It has been widely reported in literature that a higher efficiency in the dissolution of metals (either iron or aluminium) in electrocoagulation is expected with chloride because this anion has the ability to locally dissolve the passive layer that can be formed during the process^{24, 33}. Thus, these results means that no passive layers are formed under the experimental conditions and the time frame of the tests performed in this work.

One of the most important parameters to control in real drinking water treatment processes is pH, a variable that should be kept close to neutrality. The evolution of this

variable is gathered in Figure 4, which represents the pH at the outlet of the ECU device (Figure 4.a) compared to the pH after dosing the same concentration of iron as FeCl_3 , (Figure 4.b).

Fig. 4. Comparison of final pH change of ECU (4.a) and conventional coagulation (4.b) for similar iron dosing. • 100 $\mu\text{S cm}^{-1}$; ▲ tap water; ♦ 1000 $\mu\text{S cm}^{-1} \text{SO}_4^{2-}$; ■ 1000 $\mu\text{S cm}^{-1} \text{Cl}^-$

As it can be observed in Figure 4.a, the change in the pH for the ECU device is almost negligible except for the solution of the lowest conductivity, in which the value of the pH slightly increased from 7 to 9.5, which may be explained in terms of the lower ionic strength of this water and, in turn, can be one of the causes of the higher iron production. For the rest of the tests of the ECU device, the evolution of pH with applied electric charge is practically coincident. This evolution of pH can be explained in terms of the reactions of water oxidation and reduction (Equations 2 and 3 respectively) ³⁴. Equation (2) is a competitive reaction with iron dissolution at the anode and the main responsible of the loss of efficiency of the process, meanwhile reaction of water reduction (Equation 3) is the main reaction occurring at the cathode. Moreover, the precipitation of iron hydroxide from the iron dosed, according to Equation (4), is occurring simultaneously. All together

explains that in many different matrixes the value of pH in electrocoagulation process tends to stabilize in slightly basic values^{33, 35}.

On the contrary, the chemical addition of FeCl_3 to the solution causes a decrease of the pH in the entire range of conductivities tested. The decrease in the pH was less accused for tap water due to the well-known buffer capacity of carbonates. For the rest of tests, the final pH was lower than 4 after adding a dose of iron equivalent to that dosed electrochemically, due to the formation of iron (III) hydroxide by means of equation (4), among other iron species of dissimilar solubility ($\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3^-$, etc.)³⁶. All of these reactions result in the formation of H^+ and thus reduce the pH of the solution. This is one of the key advantages of the electrochemical dosing of iron compared to the conventional chemical addition of iron salts. In this latter case, a subsequent neutralization step should be required to allow an efficient use of the coagulant, as it is well-known that the efficiency of the coagulation process dramatically decreases for lower pH values due to the higher solubility of iron species. As a consequence, this would increase the economic and environmental impact of the treatment by chemical coagulation.

Next, both processes (electrochemical and chemical dosing) were compared in terms of conductivity, an additional key variable to be controlled in real drinking treatment processes. As it is commented in the experimental section, a neutralization step was carried out after the addition of iron in order to simulate a real treatment process in the

case of chemical dosing of FeCl_3 . The results (expressed as the ratio of final vs initial conductivity) are gathered in Figure 5.

Fig. 5. Comparison of relative conductivity of ECU (5.a) and conventional coagulation-neutralization (5.b) for similar iron dosing. • 100 $\mu\text{S cm}^{-1}$; ▲ tap water; ♦ 1000 $\mu\text{S cm}^{-1}$ SO_4^{2-} ; ■ 1000 $\mu\text{S cm}^{-1}$ Cl^- . Neutralization by adding NaOH.

As it is observed, the electrochemical dosing of iron provokes a slight decrease in the conductivity, being the relative decline observed in this parameter higher for lower initial conductivity. In many works, it has been reported the capacity of iron precipitates to remove a wide variety of ions mainly by adsorption on the growing flocs^{11, 18, 37-39}. In the case of chemical dosing-neutralization, an increase in the relative conductivity of the effluent was observed for all the effluents tested except for the tap water. In these cases, the addition of ions in the form of FeCl_3 and sodium hydroxide (in the neutralization stage) overcomes the flocs ability to adsorb the ions present in the solution. The exception in this behaviour of tap water is expected due to the lowest decrease in the pH previously explained in the stage of iron dosing, which requires a negligible addition of sodium hydroxide to neutralize the solution.

Finally, in order to compare the chemical speciation of the iron dosed in both systems, Figure 6 shows the redox potential at the outlet of the ECU device (Figure 6.a) and after a comparable chemical dosing of iron and neutralization (Figure 6.b).

Fig. 6. Comparison of final redox potential of ECU (6.a) and conventional coagulation-neutralization (6.b) for similar iron dosing. • $100 \mu\text{S cm}^{-1}$; ▲ tap water; ♦ $1000 \mu\text{S cm}^{-1} \text{SO}_4^{2-}$; ■ $1000 \mu\text{S cm}^{-1} \text{Cl}^-$. Neutralization by adding NaOH.

Figure 6 shows the dissimilar behaviour of both systems in terms of final redox potential. In the case of the ECU device, there exists a decrease in the redox potential for increasing the applied charge. This decrease in the redox potential means a higher reductive capacity of the effluent, what can be directly related to a higher $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio⁴⁰. In the case of chemical dosing, the redox potential remains positive, indicating a high proportion of Fe^{3+} in the iron speciation.

As it is widely known, chemical dosing of iron in a coagulation process should be performed under energetic agitation, giving a solution saturated in oxygen. In a saturated solution and at pH values over 5, the quick oxidation of Fe^{2+} to Fe^{3+} by dissolved oxygen (Equation 5) is performed with high efficiency^{41, 42}. In the case of the ECU unit, the

solution is not directly in contact with atmospheric air so it should be expected that the amount of dissolved oxygen might be lower than in a stirred tank used in conventional coagulation. Although the potential Fe^{2+} dosed in the ECU unit would be quickly oxidized to Fe^{3+} once it exists the cell, this potential formation of Fe^{2+} could extent the application of the ECU device to applications different from electrocoagulation, as it is the case of water treatment by the Fenton related processes.

4. Conclusions.

The following conclusions can be obtained from the present work:

- The novel ECU cell presented in the present work is an efficient and easy-to-use electrochemical device capable to produce and dose the iron species needed in the pre-treatment of surface water sources. It can be successfully used with water matrixes with ionic conductivities within the range $100 \mu\text{S cm}^{-1}$ - $1000 \mu\text{S cm}^{-1}$.
- The presented cell overcomes the behaviour of a conventional chemical dosing (in the form of FeCl_3) because it attains a better pH control and it produces a decrease in the effluent conductivity.
- The coagulant provided by the ECU device have a high ration of Fe^{2+} , widen the potential application to Fenton related processes.

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References

1. Nidheesh PV and Singh TSA, Arsenic removal by electrocoagulation process: Recent trends and removal mechanism. *Chemosphere* **181**: 418-432 (2017).
2. Vasudevan S, Lakshmi J and Sozhan G, Studies on the removal of arsenate by electrochemical coagulation using aluminum alloy anode. *Clean - Soil, Air, Water* **38**: 506-515 (2010).
3. Llanos J, Cotillas S, Cañizares P and Rodrigo MA, Electrocoagulation as a key technique in the integrated urban water cycle—A case study in the centre of Spain. *Urban Water Journal* **14**: 650-654 (2017).
4. Kobya M, Akyol A, Demirbas E and Oncel MS, Removal of arsenic from drinking water by batch and continuous electrocoagulation processes using hybrid Al-Fe plate electrodes. *Environmental Progress and Sustainable Energy* **33**: 131-140 (2014).
5. Gandhimathi R, Babu A, Nidheesh PV, Ramesh ST and Anantha Singh TS, Laboratory study on leachate treatment by electrocoagulation using fly ash and bottom ash as supporting electrolytes. *Journal of Hazardous, Toxic, and Radioactive Waste* **19** (2015).
6. Elabbas S, Ouazzani N, Mandi L, Berrekhis F, Perdicakis M, Pontvianne S, Pons MN, Lapique F and Leclerc JP, Treatment of highly concentrated tannery wastewater using electrocoagulation: Influence of the quality of aluminium used for the electrode. *Journal of Hazardous Materials* **319**: 69-77 (2016).
7. Kobya M, Hiz H, Senturk E, Aydinler C and Demirbas E, Treatment of potato chips manufacturing wastewater by electrocoagulation. *Desalination* **190**: 201-211 (2006).
8. Valero D, Ortiz JM, García V, Expósito E, Montiel V and Aldaz A, Electrocoagulation of wastewater from almond industry. *Chemosphere* **84**: 1290-1295 (2011).
9. Akyol A, Treatment of paint manufacturing wastewater by electrocoagulation. *Desalination* **285**: 91-99 (2012).
10. Pouet MF and Grasmick A, Urban wastewater treatment by electrocoagulation and flotation. *Water Science and Technology* **31**: 275-283 (1995).
11. Elazzouzi M, Haboubi K and Elyoubi MS, Electrocoagulation flocculation as a low-cost process for pollutants removal from urban wastewater. *Chemical Engineering Research and Design* **117**: 614-626 (2017).
12. Makwana AR and Ahammed MM, Electrocoagulation process for the post-treatment of anaerobically treated urban wastewater. *Separation Science and Technology (Philadelphia)* **52**: 1412-1422 (2017).
13. Rodrigo MA, Cañizares P, Buitrón C and Sáez C, Electrochemical technologies for the regeneration of urban wastewaters. *Electrochimica Acta* **55**: 8160-8164 (2010).
14. Feng Y, Yang L, Liu J and Logan BE, Electrochemical technologies for wastewater treatment and resource reclamation. *Environmental Science: Water Research and Technology* **2**: 800-831 (2016).
15. Liu Z, Stromberg D, Liu X, Liao W and Liu Y, A new multiple-stage electrocoagulation process on anaerobic digestion effluent to simultaneously reclaim water and clean up biogas. *Journal of Hazardous Materials* **285**: 483-490 (2015).
16. Garcia-Segura S, Eiband MMSG, de Melo JV and Martínez-Huitle CA, Electrocoagulation and advanced electrocoagulation processes: A general review

- about the fundamentals, emerging applications and its association with other technologies. *Journal of Electroanalytical Chemistry* **801**: 267-299 (2017).
17. Cañizares P, Jiménez C, Martínez F, Sáez C and Rodrigo MA, Study of the electrocoagulation process using aluminum and iron electrodes. *Industrial and Engineering Chemistry Research* **46**: 6189-6195 (2007).
 18. Mamelkina MA, Cotillas S, Lacasa E, Sáez C, Tuunila R, Sillanpää M, Häkkinen A and Rodrigo MA, Removal of sulfate from mining waters by electrocoagulation. *Separation and Purification Technology* **182**: 87-93 (2017).
 19. Cañizares P, Jiménez C, Martínez F, Rodrigo MA and Sáez C, The pH as a key parameter in the choice between coagulation and electrocoagulation for the treatment of wastewaters. *Journal of Hazardous Materials* **163**: 158-164 (2009).
 20. Bayramoglu M, Eyvaz M and Kobya M, Treatment of the textile wastewater by electrocoagulation. Economical evaluation. *Chemical Engineering Journal* **128**: 155-161 (2007).
 21. Sasson MB, Calmano W and Adin A, Iron-oxidation processes in an electroflocculation (electrocoagulation) cell. *Journal of Hazardous Materials* **171**: 704-709 (2009).
 22. Jiménez C, Sáez C, Cañizares P and Rodrigo MA, Optimization of a combined electrocoagulation-electroflotation reactor. *Environmental Science and Pollution Research* **23**: 9700-9711 (2016).
 23. Gamage NP, Rimer JD and Chellam S, Improvements in permeate flux by aluminum electroflotation pretreatment during microfiltration of surface water. *Journal of Membrane Science* **411-412**: 45-53 (2012).
 24. Llanos J, Cotillas S, Cañizares P and Rodrigo MA, Effect of bipolar electrode material on the reclamation of urban wastewater by an integrated electrodisinfection/electrocoagulation process. *Water Research* **53**: 329-338 (2014).
 25. Moussa DT, El-Naas MH, Nasser M and Al-Marri MJ, A comprehensive review of electrocoagulation for water treatment: Potentials and challenges. *Journal of Environmental Management* **186**: 24-41 (2017).
 26. Arenas LF, Ponce de León C and Walsh FC, 3D-printed porous electrodes for advanced electrochemical flow reactors: A Ni/stainless steel electrode and its mass transport characteristics. *Electrochemistry Communications* **77**: 133-137 (2017).
 27. Wang L, Zhao Y, Gao Q, Qian C and Hu Y, A new strategy for determination of current efficiency during electro-oxidation of aromatic compounds in a packed-bed system. *Water Science and Technology* **63**: 2685-2691 (2011).
 28. Ren G, Zhou M, Liu M, Ma L and Yang H, A novel vertical-flow electro-Fenton reactor for organic wastewater treatment. *Chemical Engineering Journal* **298**: 55-67 (2016).
 29. Ma L, Zhou M, Ren G, Yang W and Liang L, A highly energy-efficient flow-through electro-Fenton process for organic pollutants degradation. *Electrochimica Acta* **200**: 222-230 (2016).
 30. Moreno-Casillas HA, Cocke DL, Gomes JAG, Morkovsky P, Parga JR and Peterson E, Electrocoagulation mechanism for COD removal. *Separation and Purification Technology* **56**: 204-211 (2007).
 31. Parga JR, Cocke DL, Valverde V, Gomes JAG, Kesmez M, Moreno H, Weir M and Mencer D, Characterization of electrocoagulation for removal of chromium and arsenic. *Chemical Engineering and Technology* **28**: 605-612 (2005).

32. Cañizares P, Carmona M, Lobato J, Martínez F and Rodrigo MA, Electrodeposition of aluminum electrodes in electrocoagulation processes. *Industrial and Engineering Chemistry Research* **44**: 4178-4185 (2005).
33. Mansouri K, Elsaid K, Bedoui A, Bensalah N and Abdel-Wahab A, Application of electrochemically dissolved iron in the removal of tannic acid from water. *Chemical Engineering Journal* **172**: 970-976 (2011).
34. Mollah MYA, Morkovsky P, Gomes JAG, Kesmez M, Parga J and Cocke DL, Fundamentals, present and future perspectives of electrocoagulation. *Journal of Hazardous Materials* **114**: 199-210 (2004).
35. Aoudj S, Khelifa A and Drouiche N, Removal of fluoride, SDS, ammonia and turbidity from semiconductor wastewater by combined electrocoagulation–electroflotation. *Chemosphere* **180**: 379-387 (2017).
36. Hakizimana JN, Gourich B, Chafi M, Stiriba Y, Vial C, Drogui P and Naja J, Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. *Desalination* **404**: 1-21 (2017).
37. Kim JH, Maitlo HA and Park JY, Treatment of synthetic arsenate wastewater with iron-air fuel cell electrocoagulation to supply drinking water and electricity in remote areas. *Water Research* **115**: 278-286 (2017).
38. Lacasa E, Cañizares P, Sáez C, Fernández FJ and Rodrigo MA, Removal of nitrates from groundwater by electrocoagulation. *Chemical Engineering Journal* **171**: 1012-1017 (2011).
39. Jadhav SV, Bringas E, Yadav GD, Rathod VK, Ortiz I and Marathe KV, Arsenic and fluoride contaminated groundwaters: A review of current technologies for contaminants removal. *Journal of Environmental Management* **162**: 306-325 (2015).
40. Gadd A, Ryan D, Kavanagh J, Beaurain AL, Luxem S and Barton G, Electrocoagulation of fermentation wastewater by low carbon steel (Fe) and 5005 aluminium (Al) electrodes. *Journal of Applied Electrochemistry* **40**: 1511-1517 (2010).
41. Lakshmanan D, Clifford DA and Samanta G, Ferrous and ferric ion generation during iron electrocoagulation. *Environmental Science and Technology* **43**: 3853-3859 (2009).
42. Xu X and Zhu X, Treatment of refractory oily wastewater by electro-coagulation process. *Chemosphere* **56**: 889-894 (2004).