

Design and optimization Optimization of a combined electrocoagulation-electroflotation reactor **for wastewater** **treatment**

C. Jiménez, C. Sáez, P. Cañizares, M.A. Rodrigo*

Department of Chemical Engineering. Universidad de Castilla La Mancha, Campus

Universitario 12. E13071 Ciudad Real. Spain; Fax: +34 926 29 52 56; Tel: +34 926 29 53

00; E-mail: Manuel.Rodrigo@uclm.es

Abstract

This work studies the efficiency of an electroflotation process for the separation of the solids produced during the electrocoagulation treatment of three different types of wastewater: kaolin suspension, coloured organic solution and oil-in-water emulsion. Additionally, a combined electrocoagulation-electroflotation reactor is designed and optimized taking into account the effect of current density, residence time, pollutant concentration and the ratio floated/settled solids. To do this, an experimental design with response surface methodology (RSM) has been used. Results show that electroflotation is a good alternative to the removal of oil microdrops and dyes but it is not recommended for the separation of solids formed during **electro**coagulation of colloids suspensions due to its high density. It has been found that the use of aluminium leads to better results than the use of iron in the treatment of oil-in-water emulsions and coloured solutions. In these cases, the use of a combined

electrocoagulation-electroflotation reactor is recommended and the effect of the main inputs has been studied.

Keywords: emulsion; suspension; dye; electrocoagulation; electroflotation; RSM

Highlights

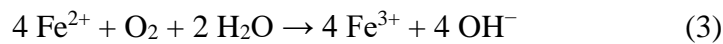
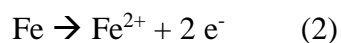
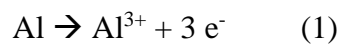
- Combined electrocoagulation - electroflotation is very efficient for low-density flocs.
- Aluminium electrocoagulation leads to better electroflotation of oil-in-water emulsions than iron electrocoagulation.
- Removal of dyes flocs by electroflotation is faster when aluminium is used as coagulant but the total removal attained is comparable to that obtained with iron.
- Electrocoagulation and electroflotation can be successfully combined in a single prototype
- RSM models successfully the results obtained in a combined electrocoagulation-electroflotation reactor

1. Introduction

The use of electricity for wastewater treatment was proposed for the first time in United Kingdom in 1889 (Strokach 1975). However, the electrocoagulation with aluminium and iron electrodes was not applied at the full-scale till 1946, when it was proposed for the treatment of supply water (Bonilla 1947, Stuart 1946). The experience was not positive and the high investment and electricity costs prevented against the further use of these technologies. Consequently, till the end on the 20th century, these environmental electrochemical technologies were almost forgotten. In that moment, because of the significant increase in the standards required for supply water and, as well, because of the day-to-day stricter environmental regulations related to wastewater discharges, the electrochemical technologies, and among them electrocoagulation and electroflotation, have become again promising technologies.

In the last years, several works have been focused on the study of the electrocoagulation-electroflotation process and its applications as an alternative to conventional coagulation-flocculation technology. Interesting researches (Holt et al. 2002, Merzouk et al. 2010, Zodi et al. 2009, 2010, 2013, Zongo et al. 2009a, Zongo et al. 2009b) have demonstrated that electrocoagulation technology is competitive for the removal of pollutants from supply water, urban wastewater and for the treatment of industrial effluents, such as those produced in food-manufacturing or textile industries. In the same way, the electroflotation has been successfully applied for the removal of suspended matter (Ahmed & Jameson 1985, Ketkar et al. 1991) and for the breaking-up of oil-in-water emulsions (Hosny 1992, Khemis et al. 2006).

Electrocoagulation consists of the in situ generation of coagulants through electrochemical oxidation of an appropriate anode material, such as aluminium or iron. Therefore, the main reaction that occurs in the electrochemical cell is the anode oxidation (equations 1 and 2). In neutral or alkaline media, Fe^{2+} ions are oxidized to Fe^{3+} because of the oxygen dissolved in water (equation 3) (Chen 2004).



Fe^{3+} and Al^{3+} get hydrolysed in water, dealing to the generation of different coagulant species (Holt et al. 2002, Jimenez et al. 2012):

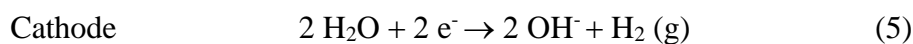
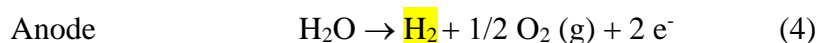
- insoluble hydroxides above which can enmesh the pollutants and/or
- cationic or anionic hydroxocomplexes, that destabilize the electrostatic repulsion forces that exist in colloidal matter (or in the droplets of an oil-in-water emulsion), due to a charge neutralization mechanism or due to bond formation between particles.

In addition to the in-situ production of coagulants, some other processes occur inside the electrochemical cell with a great importance in the global electrocoagulation process. Therefore, close to the anode, oxygen generation due to water oxidation deals to the formation of H^+ ions that, because of their charge, are attracted to the cathode. In the cathode, water reduction to hydrogen deals to the generation of hydroxyl ions (OH^-) that are attracted to the anode. Consequently, a pH profile is generated between each anode and cathode inside the cell, which favours the production of different chemical species inside the reactor from the species produced in the anode and that different simultaneous processes take part in the global

electrochemical process. According to literature (Mollah et al. 2001, Rajeshwar & Ibañez 1997), this pH profile can explain the lowest coagulant concentration required during the electrochemical treatment for achieving the same efficiency as compared to the conventional physicochemical coagulation process.

One of the main advantages of the electrocoagulation process is that the gases produced in the electrodes surface can adhere to the flocs formed reducing their density and allowing them to be separated by flotation. This process is known as electroflotation and is a secondary process in every electrocoagulation treatment. However, sometimes it can be used as a separate process for the removal of solids contained in water.

Electroflotation is a simple process that consists of floating the particulate pollutants of water or wastewater by the action of the tiny bubbles of hydrogen and oxygen produced during water electrolysis (Jimenez et al. 2010, Raju & Khangaonkar 1984). Dimensionally stable anodes (DSA), platinum, graphite, titanium or stainless steel are usually employed as electrodes in these processes. So, when current is applied, it is achieved the generation of oxygen in the anode and hydrogen in the cathode, according to equations 4 and 5.



The most important uses of technologies based on flotation processes in wastewater treatment are greases and oil removal, fibbers and light particles removal and sludge thickening. The principles of flotation are simple: tiny air bubbles get adhere to the particles of pollutant, and the decrease in the density of the group particle-bubble, down to values below that of water, makes it rise to the liquid surface. The main advantage of flotation as compared to

sedimentation is that it enhances the removal efficiency of the smallest or lightest particles, whose sedimentation rate is very low. Thus, every flotation process consists of two steps: the generation of bubbles and the collision of those bubbles with particles inside the reactive media. In general, the main difference between the different flotation processes consists of the way of producing the bubbles. Between the most used technologies the most important are: *aeration flotation*, that consists of the aeration at atmospheric pressure of liquid phase; *vacuum flotation*, that consists of saturating the liquid phase with air at atmospheric pressure, followed by the application of vacuum to the liquid; *dissolved air flotation (DAF)*, that consists of injecting pressured air to the liquid phase and then reducing the pressure; or *electroflotation*, that consists of producing oxygen or hydrogen microbubbles by water oxidation-reduction in the electrodes of an electrochemical cell.

The main characteristics of combined electrocoagulation-electroflotation processes are their equipment and operative simplicity, a small residence time, a low or almost null requirement of reactive addition and a lower sludge formation than conventional processes (Chen 2004). For all of these reasons, this technology appears as a promising alternative to take advantage of the combined production of polyvalent cations by oxidation of sacrificial anodes (Al or Fe) and the flotation of the pollutants to the liquid surface, where they can be collected and removed easily. Despite of the advantages reported for these technologies, there is scarce information about the reactor design, although it is expected to have a great influence on the efficiency of the process (Essadki et al. 2009). Moreover, there is not a predominant reactor design, probably because of the high complexity of these processes, that include electrochemical, coagulation and hydrodynamic processes (Holt et al. 2002). Thus, there are three predominant mechanisms in electrocoagulation-electroflotation combined processes:

- Electrodes oxidation.

- Gas bubbles formation.
- Flotation and sedimentation of the floccules.

The main objective of this work is to study the efficiency of an electroflotation (EF) process for the separation of the solids formed during previous electrocoagulation (EC) treatment of different types of wastewater. Moreover, the influence of two coagulants (aluminium and iron) during the previous electrocoagulation process, in the efficiency of the flotation step has been studied. Three different types of synthetic wastewater have been used: kaolin, as a model of suspended matter pollution; eriochrome black T (EBT), as a model of soluble organic matter pollution; and oil-in-water emulsions, as a model of emulsified pollution. In addition, a combined electrocoagulation-electroflotation (ECEF) reactor has been designed and optimized in this work. To achieve this objective, an experimental design with response surface methodology (RSM) has been used. The combination effects of current density, residence time and pollutant concentration in the removal of pollutants and in the floated/settled solids ratio have been studied, in order to find the optimum operation conditions of the reactor.

2. Materials and Methods

2.1 Experimental setups.

For this work, two different experimental lab scale plants have been used as shown in Figure 1, the first one working in batch mode (Figure 1A), and the second one working in continuous mode (figure 1B).

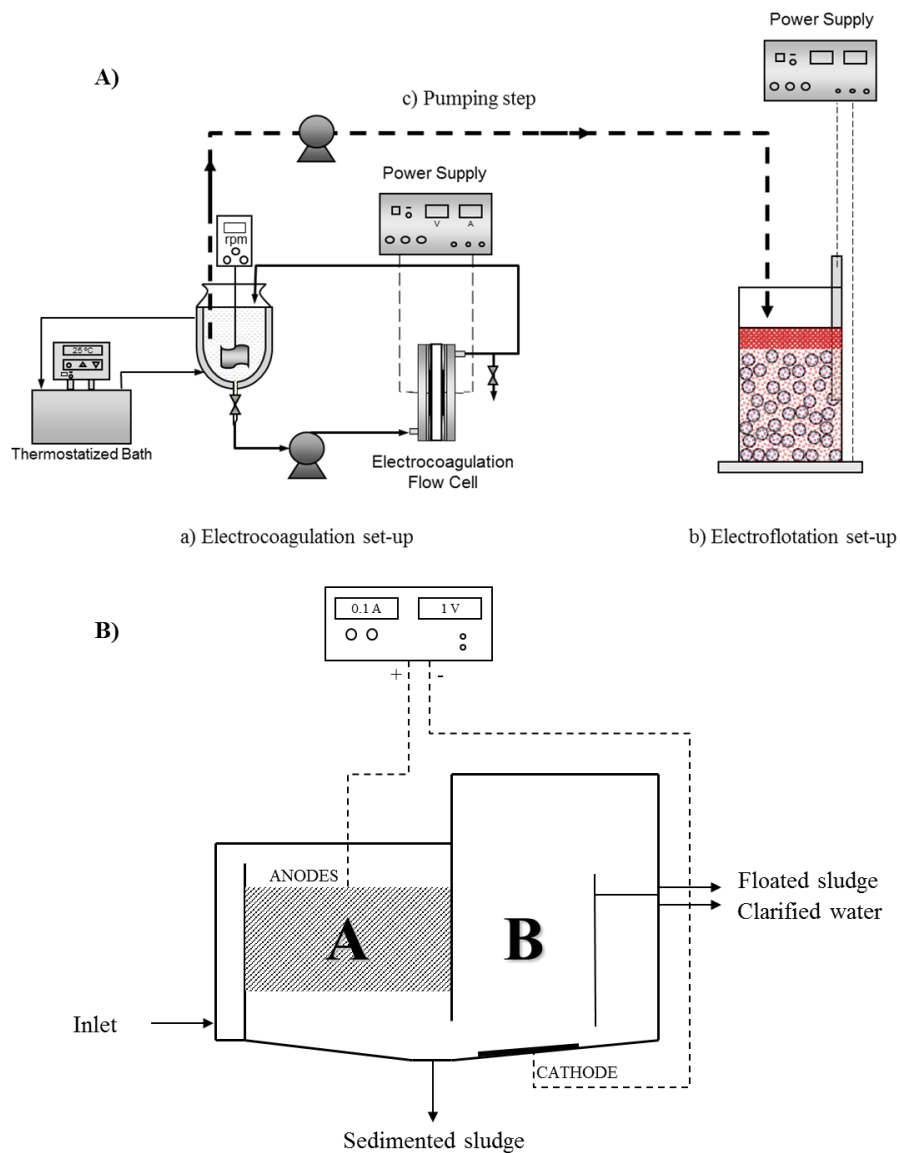


Figure 1. Experimental set-up. A) Batch mode: a) Electrocoagulation set-up; b) Electroflotation set-up; c) pumping step after the electrocoagulation (wastewater is pumped to the electroflotation set-up to remove the flocs formed). B) Experimental set-up. A: anodic zone; B: cathodic zone

Batch operation mode plant. A scheme of the whole experimental set-up is shown in Figure 1A. It consists of two units operated in batch mode: the electrocoagulation unit and the electroflotation reactor. The electrocoagulation setup consisted of a bench-scale plant, with a single-compartment electrochemical flow cell. Aluminum or iron electrodes were used as the anode and cathode. Both electrodes were square in shape with a geometric area of 100 cm^2 each and with an electrode gap of 9 mm. In every experiment, the anodic and cathodic materials were the same. The electrolyte was stored in a 5 L glass tank, stirred by an overhead stainless steel rod stirrer, Heidolph RZR 2041, thermostated by means of a water-bath to maintain the temperature at the desired set point, and circulated through the electrolytic cell by a peristaltic pump. The electroflotation cell was constructed of glass with dimensions of $10 \times 2 \times 20 \text{ cm}^3$ and it works in batch operation mode. A polished stainless steel cathode was placed in the bottom of the cell and a platinum anode was placed 13 cm above the cathode. This configuration has been chosen in order to take advantage of the hydrogen bubbles produced separately from oxygen ones.

Continuous operation mode plant. The experimental setup used for the continuous assays is a methacrylate combined electrocoagulation-electroflotation reactor shown in Figure 1B. The reactor consists of two zones. The first one includes 3-5 aluminium sheets that work as the anode of the cell to generate the coagulant species for the coagulation process. The second one includes a polished stainless steel cathode in horizontal position at the bottom of the reactor to produce hydrogen bubbles that float the flocs formed during the coagulation step to the surface of the reactor. Floated and settled solids are collected separately in order to measure total and suspended solids.

2.2. Experimental procedure

Batch operation mode. Coagulant was electrochemically added to wastewater using the electrocoagulation set-up. Electrochemical coagulation tests were carried out under galvanostatic conditions and in discontinuous operation mode. Prior to every experiment, the electrodes were rinsed with 1.30 M HCl in order to avoid any effect on results caused by the previous applications of the electrodes. For the electrochemical coagulation experiments, the pollutant solution was pumped in between the feed tank and the electrocoagulation cell. In the tank, wastewater was stirred during the experiments in order to favour the mixing of the coagulant and the pollutant particles. On having applied the required electric charge (by keeping electrolysis during the required time), the power supply was switched off while stirring was kept. The electric charge was calculated according to previous tests (Canizares et al. 2007a) and corresponds to the following electrolysis time: 25 minutes for kaolin suspension, 15 minutes for EBT solutions and 90 minutes for oil-in-water emulsions.

Once the coagulation step was completed, wastewater was pumped from the electrocoagulation to the electroflotation cell and a sample was taken to characterize the effluent of the electrocoagulation step. Then, electroflotation was applied during different times depending on the pollutant (under galvanostatic conditions and in discontinuous operation mode) and another sample was taken from the reactor. The electric charge selected was that which allows obtaining the tiniest hydrogen bubbles, according to previous tests (Jimenez et al. 2010). Finally, the solution was allowed to settle for 30 min. A third sample was taken then, after sedimentation.

Continuous operation mode. Response surface methodology (RSM). RSM has been used to optimize the operating conditions in a combined continuous ECEF reactor. According to

literature, RSM is considered an effective way of reducing the experimental assays needed when a process has to be optimized and it can be used to determine the statistical significance of the different variables studied and their interactions and to build models (Chavalparit & Ongwande 2009, Gurses et al. 2002, Tir & Moulai-Mostefa 2008).

In this work, the effect of three operational variables: current density (x_1), residence time of the reactor (x_2) and pollutant concentration (x_3) have been studied using a 2^3 experimental design combined with a star design using four replicates of the central point. For the star design, half of the range of the experimental design has been taken. Experimental data was fitted to a second order polynomial model when the results lead to a non-linear system or to a first order polynomial model if they lead to a linear system, and the regression coefficients a_0 , a_i , a_{ii} and a_{ij} were obtained in each case (equations 6 and 7) by mathematical fitting. In these equations x_i , x_j and x_{ii} are the inputs and Y_i are the outputs. Y_1 indicates the efficiency of the process for pollutants removal, and Y_2 is the floated/settled solids ratio. Both parameters are of great importance as the main objective of this work is to remove pollutants from wastewater trying to optimize the electroflotation inside the reactor. More details about the RSM are shown in the supplementary materials.

$$Y_i = a_0 + \sum_{i=1}^3 a_i x_i + \sum_{i=1}^3 a_{ii} x_{ii}^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 a_{ij} x_i x_j \quad (6)$$

$$Y_i = a_0 + \sum_{i=1}^3 a_i x_i + \sum_{i=1}^2 \sum_{j=i+1}^3 a_{ij} x_i x_j \quad (7)$$

2.3. Characterization Techniques.

The electrical current has been applied using a Promax FA-376 DC power supply. The potential and the current flowing through the cell have been measured with a Keithley 2000 digital multimeter. Depending on the type of pollutant studied, different parameters have been measured:

- Kaolin suspensions: Turbidity (using a 115 VELP SCIENTIFICA Turbidimeter) and pH (using an inoLab WTW pH meter) were measured in the clarified liquid while total and suspended solids were measured for both floated and settled solids (Clesceri et al. 1998).
- EBT solutions: samples were first filtered and then the absorbance spectrum (using a UV – visible spectrophotometer Shimadzu UV-1603), chemical oxygen demand (COD; using a Hach DR2000 analyzer) and pH were measured in the clarified water. Volatile solids concentration was measured for the floated and the settled sludge samples (total solids could not be measured as the EBT concentration is much lower than the electrolyte concentration, so it interferes in the measurement).
- Oil-in-water emulsions: Turbidity, COD and pH were measured in the aqueous phase. Total solids concentration was measured for the floated and the settled sludge samples.

For measuring the roughness of the cathodic sheet during the electroflotation assays, a surface roughness tester (PCE-RT 1200) was used. The roughness parameter measured was arithmetical mean deviation of profile within sampling length (defined as Ra).

3. Results and discussion

Batch operation mode tests. Electrocoagulation is a complex technology which involves processes as different as the destabilization of suspensions or emulsions or the precipitation of species contained in a solution. It transforms colloids, microdrops or dissolved pollutants into flocs, which can be separated from wastewater by sedimentation or flotation. Taking into account the very different nature of these particles, in order to study the efficiency of electroflotation in the separation of the solids formed during electrochemical coagulation processes, some electrocoagulation and electroflotation assays have been carried out using three models of wastewater previously characterized by our group (Canizares et al. 2006, 2007b, Canizares et al. 2008): kaolin suspensions, eriochrome black T solutions and oil-in-water emulsions. Furthermore, both aluminium and iron have been used as coagulants in the electrochemical assisted coagulation step, in order to evaluate whether the coagulant exhibits any influence on the separation efficiency of the flocs formed during the process. As the electrocoagulation of these three models of wastewater was exhaustively characterized, discussion of results will only focus on the electroflotation using for electrocoagulation the best conditions found in the previous studies.

Figure 2 shows the changes in the turbidity during the electroflotation of the electrocoagulated kaolin suspensions obtained with the application of a current density of 0.5 mA cm^{-2} for 25 minutes (temperature: $25 \text{ }^{\circ}\text{C}$) (optimum conditions according to a previous study) (Canizares et al. 2007b). Turbidity is a measurement of the colloid concentration contained in wastewater and not of the particles formed by electrocoagulation. Then, removal of turbidity means that floc enmeshment is promoted during the electroflotation while increase of turbidity has to be related to the destruction of the flocs formed during the previous electrocoagulation. Electroflotation experimental conditions were those that allow obtaining the tiniest hydrogen bubbles, optimized in a previous work (Jimenez et al. 2010).

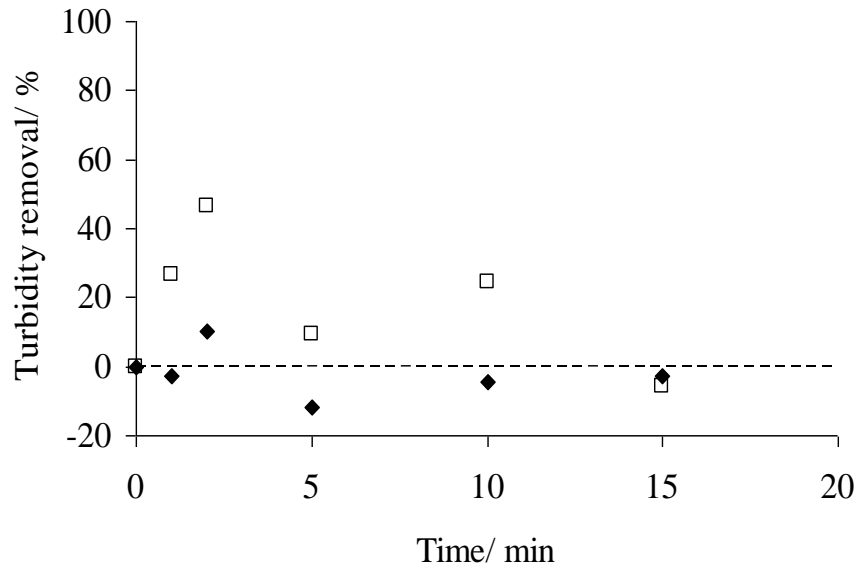


Figure 2. Changes in the turbidity removal during the electroflotation of an electrocoagulated kaolin suspension (1000 mg/L kaolin and 3000 mg/L NaCl at pH 4.5) with \blacklozenge aluminium, \square iron anodes ; initial volume: 1.5 dm³; time: 25 min. Electroflotation conditions: current density: 2.5 mA cm⁻²; temperature: 25 °C; cathode: stainless steel (Ra: 0.30).

As it can be observed, electroflotation seems to have a very small positive effect on the removal of turbidity in kaolin suspensions coagulated with iron and slightly negative (almost neutral) when the coagulant applied is aluminium. This observation can be explained by the bulkier sludge formed with iron and the much lower solubility of this coagulant that helps entrapping small colloid particles into the formed flocs. On the contrary, the higher solubility of aluminium make that flocs formed are less capable of enmeshing colloids. The high density of the flocs formed makes them to settle better than float and this explains that at the end of the test lower removals than those obtained by single electrocoagulation were obtained. The desestabilization of colloids is rapid and hence electroflocculation promoted by bubbles seems not to have a significant effect.

Electrocoagulation is also very applied in the removal of dyes from the waste solutions in which they are typically contained. Figure 3 shows the changes in the dye concentration (quantified as removal of visible light absorbance measured at 550 nm) during the electroflotation of an EBT dye solution previously electrocoagulated for 15 minutes at a current density of 1.4 mA cm^{-2} (temperature of $25 \text{ }^{\circ}\text{C}$) (optimum conditions found in a previous study for this type of waste) (Canizares et al. 2006).

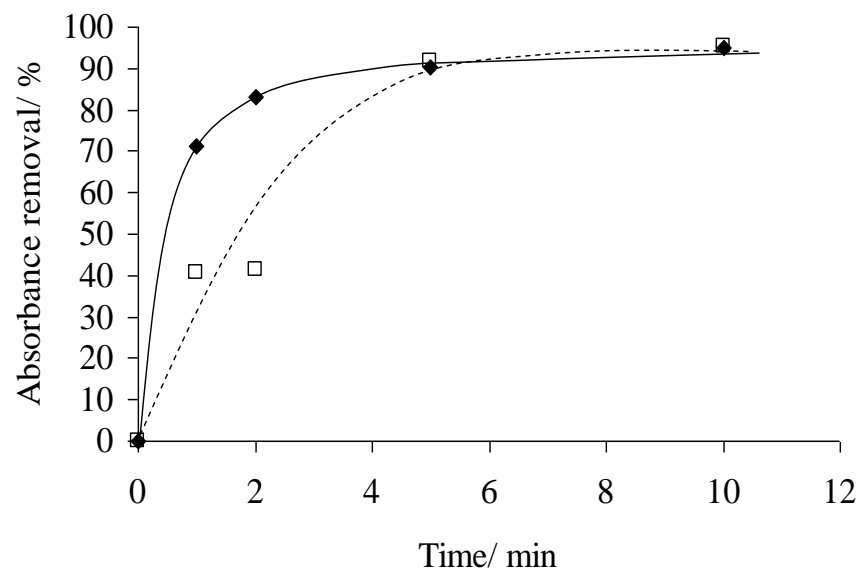


Figure 3. Absorbance removal during the electroflotation of a previously electrocoagulated eriochrome black T solution (100 mg/L of EBT and 3000 mg/L NaCl at pH 4) with \blacklozenge aluminium, \square iron anodes. Electroflotation conditions: current density: 2.5 mA cm^{-2} ; temperature: $25 \text{ }^{\circ}\text{C}$; cathode: stainless steel (Ra: 0.30).

In this case, opposite to what it was observed for the removal of colloids, absorbance removal efficiency above 90% is obtained after the electroflotation process, regardless of the coagulant type dosed in the previous electrocoagulation stage. However, colour removal is faster when aluminium is used as coagulant during the electrocoagulation process. With this electrode, in just 2 minutes colour removal efficiencies above 80% are obtained. This fact can be explained

in terms of the higher solubility of the aluminium (as compared with iron) which help to precipitate the dye non-associated to flocs and to the mixing conditions produced by bubbles that help to join this new flocs to those previously formed during the electrocoagulation stage. Nevertheless, after 5 minutes of assay, the steady state is achieved with both coagulants, and a similar efficiency is obtained.

The third model of wastewater susceptible to be coagulated is the oil-in-water emulsion. Figure 4 shows the COD removal obtained during the electroflotation of a previously electrocoagulated oil-in-water emulsions for 90 minutes at a current density of 2.2 mA cm^{-2} and keeping the temperature at $25 \text{ }^\circ\text{C}$ (optimum conditions for the treatment of this type of waste) (Canizares et al. 2008).

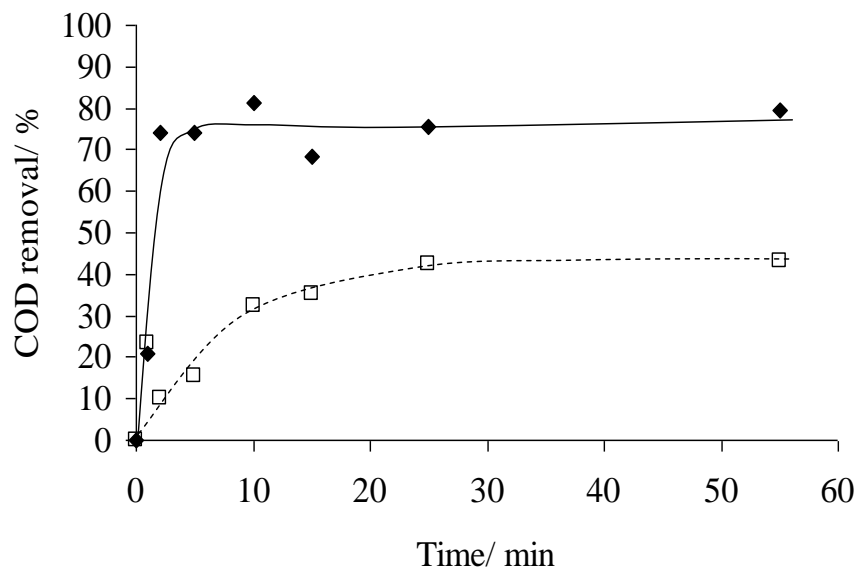


Figure 4. COD removal during the electroflotation of an electrocoagulated oil-in-water emulsion (3000 mg/L oil and 3000 mg/L NaCl at pH 4.0) with \blacklozenge aluminium and \square iron; Electroflotation conditions: current density: 2.5 mA cm^{-2} ; temperature: $25 \text{ }^\circ\text{C}$; cathode: stainless steel (Ra: 0.30).

When aluminium is used as coagulant high efficiencies are obtained for COD removal, around 80%. However, when iron is used as coagulant, electroflotation efficiency is much lower, around 40% of COD removal. This lowest efficiency of the hydrogen bubbles to remove the oil droplets produced during the electrocoagulation process can be associated to the lower concentration of free coagulant during this process, that it is related to the lower solubility.

When the electric current was stopped in the three tests bubbles were no longer produced and sedimentation starts. Table 1 compares the pollutant removal attained at the end of the electroflotation and after 30 minutes of sedimentation for the three types of wastewater tested.

Table 1. Pollutant removal percentage obtained during an electroflotation treatment and after a sedimentation process for the three types of wastewaters studied (after a previous electrocoagulation treatment with aluminium and iron).

Coagulant \ Pollutant	Aluminium		Iron	
	Flotation	Sedimentation	Flotation	Sedimentation
Kaolin	-5.8	86.2	-2.9	81.3
EBT	95.5	99.6	95.0	97.9
Emulsions	75.6	79.4	42.3	43.3

The electroflotation of wastewater polluted with kaolin does not allow us obtaining a good separation of the solids formed during the previous electrocoagulation process. On the contrary, this process slightly increases the turbidity of the solution, regardless the use of aluminium or iron during the electrocoagulation. In this case, sedimentation showed a positive influence on results and it attains turbidity removals above 80%. On the contrary, during the

treatment of wastewater polluted with EBT or oil-in-water emulsions, the sedimentation does not improve significantly the results obtained during electroflotation. For these types of pollutants, low density solids are formed during the previous electrocoagulation process, which can be easily removed using flotation techniques. Furthermore, it is observed that the removal efficiency during the treatment of oil-in-water emulsions is higher when using aluminium as electrodic material during the electrocoagulation process, due to the lower density of the aluminium flocs formed, as compared with the iron-based flocs.

Continuous operation mode tests. From the results previously obtained in this work, a combined electrocoagulation-electroflotation reactor has been developed in order to take advantage of both processes in a single reactor. To optimize the operational parameters of the reactor an experimental design analysis with **RSM** has been carried out (Kobyta et al. 2011, Korbahiti & Artut 2013, Korbahiti et al. 2011, Korbahiti & Tanyolac 2008).

The experimental design has been made for two main parameters: pollutant removal (COD has been considered in the case of EBT solutions and turbidity for kaolin suspensions and oil-in-water emulsions) and floated-settled solids ratio (total solids in the case of kaolin and emulsions and volatile solids in the case of EBT solutions). Because of the previously obtained better results for electroflotation with aluminium, this anode was selected to optimize the combined electrocoagulation-electroflotation reactor.

According to the RSM, tests were carried out to clarify the influence of the different inputs on pollutant removal and floated/settled solids ratio and results were fitted to a second order polynomial model and the regression coefficients.

Thus, Figure 5 shows the response surface for turbidity removal as a function of current density and residence time for three different values of kaolin concentration tested.

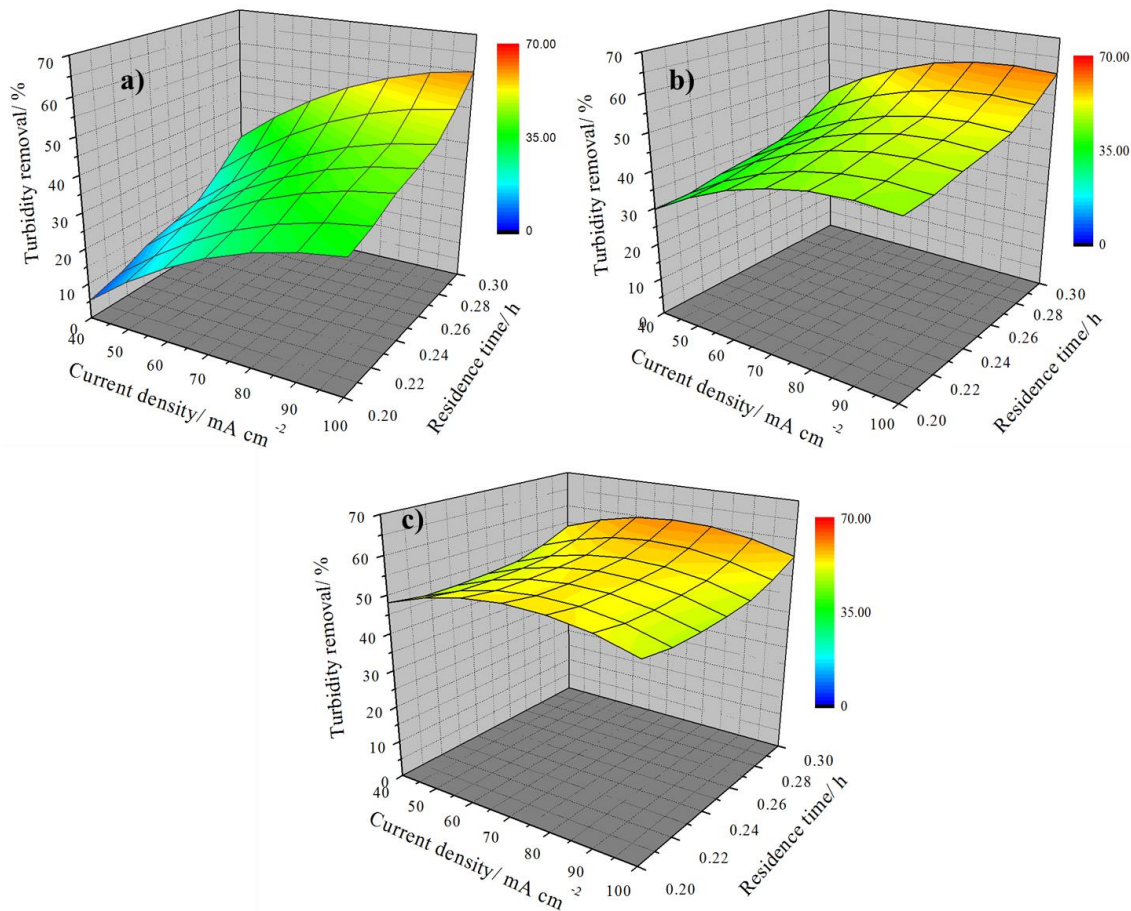


Fig. 5 Response Surface for turbidity removal when using kaolin as a model of pollutant. kaolin concentration: a) [kaolin] 500 mg/L, b) [kaolin] 1000 mg/L, c) [kaolin] 1500 mg/L

Removal efficiency increases with current density and residence time, because both parameters allow increasing the aluminium concentration in the reactor. However, the maximum turbidity removal is around 60%. Furthermore, when increasing kaolin concentration, the removal efficiency increases for low current densities and residence times as the flocculation process is favoured when increasing the number of particles in solution. For the higher kaolin concentration a flatter profile for turbidity removal is obtained with maximum removal efficiency for a current density of 2 mA cm⁻².

In Figure 6, COD removal is represented as a function of current density and residence time for three different values of initial EBT concentration tested.

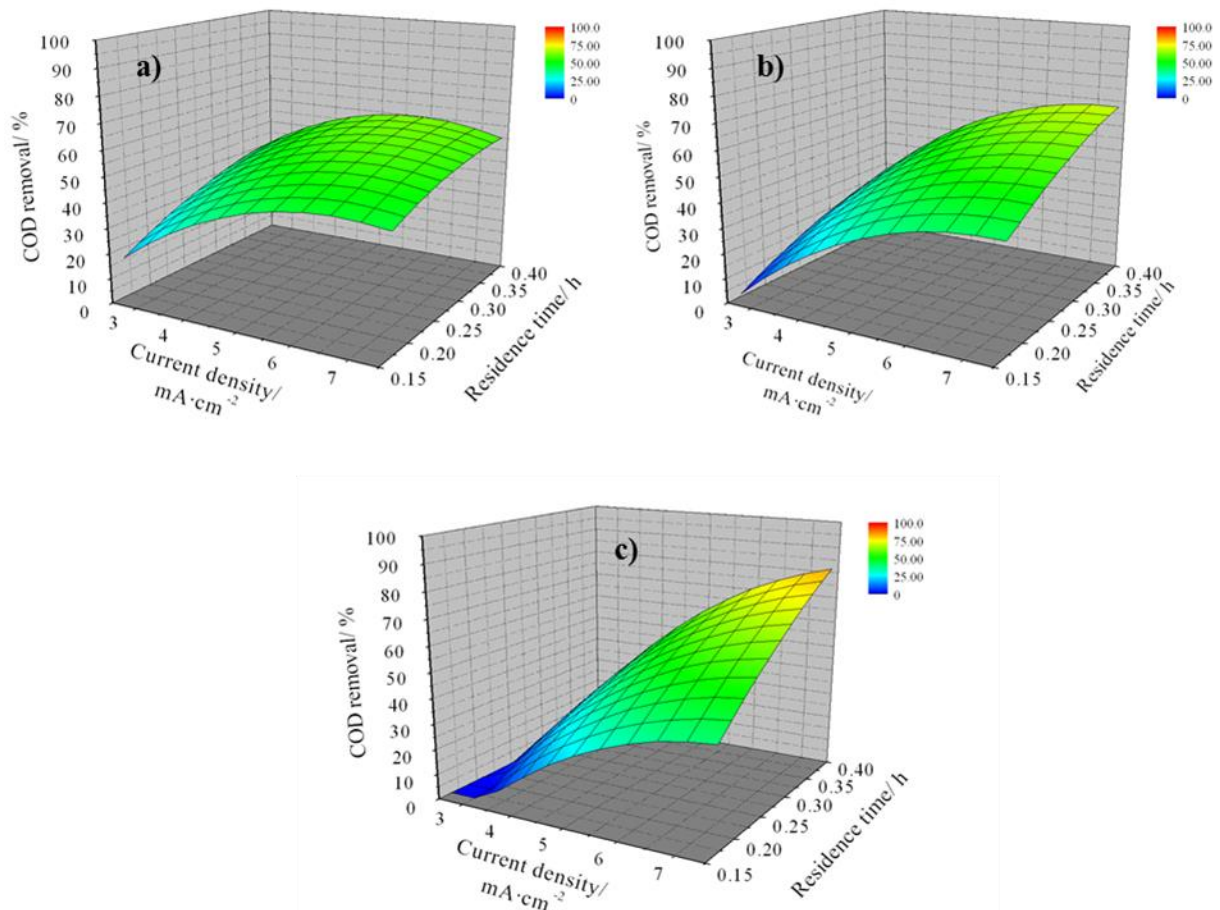


Fig. 6 Response Surface for COD removal when using EBT as a model of pollutant. EBT concentration: a) 50 mg/L; b) 150 mg/L; c) 250 mg/L

As it can be observed, the maximum removal efficiency is obtained for highest current densities and residence times, around 80% of COD removal. Moreover, this maximum value increases when increasing initial pollutant concentration. This effect can be explained because when increasing initial pollutant concentration, the flocculation process is promoted, as there are more particles in solution that can form larger flocs. On the contrary, for the lowest current density and resident time values, the removal efficiency is lower when EBT

concentration increases. This decrease in removal efficiency can occur because in those conditions the coagulant concentration is too low to produce the coagulation of the EBT. This demonstrates the importance of an adequate coagulant-pollutant concentration ratio during the coagulation step.

During the treatment of oil-in-water emulsions (Figure 7) it can be seen a comparable behaviour, with the maximum removal efficiency for the highest current density and residence time. For low values of oil concentration, turbidity removal is around 100% for every current density and residence time studied. When increasing oil concentration turbidity removal decreases for the lowest values of current density and residence time and increases linearly with both parameters, as in these conditions aluminium concentration increases too in reaction media.

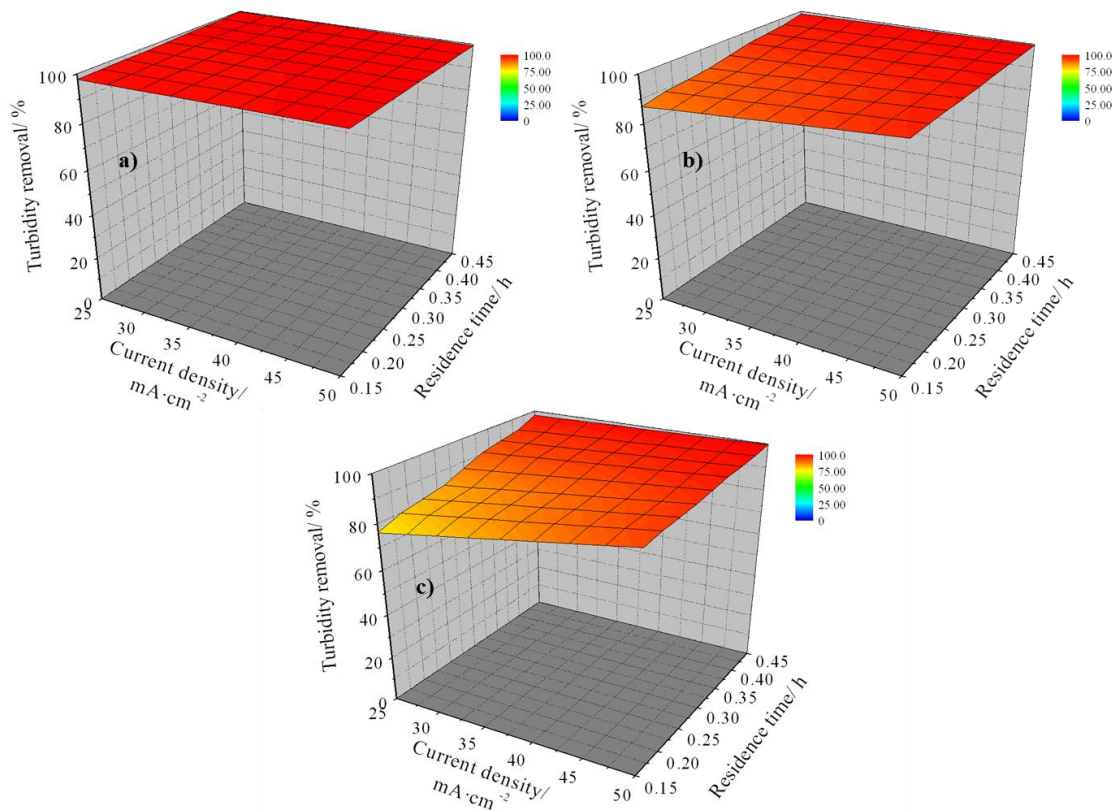


Fig. 7 Response Surface for turbidity removal when using O/W emulsions as a model of pollutant. Oil concentration: a) 1000 mg/L; b) 3000 mg/L; c) 5000 mg/L

The Response Surfaces for floated-sedimented solids ratio are shown for Kaolin (Figure 8), EBT (Figure 9) and oil-in-water emulsions (Figure 10) assays. This relationship represents the efficiency of the flotation process compared with the sedimentation one.

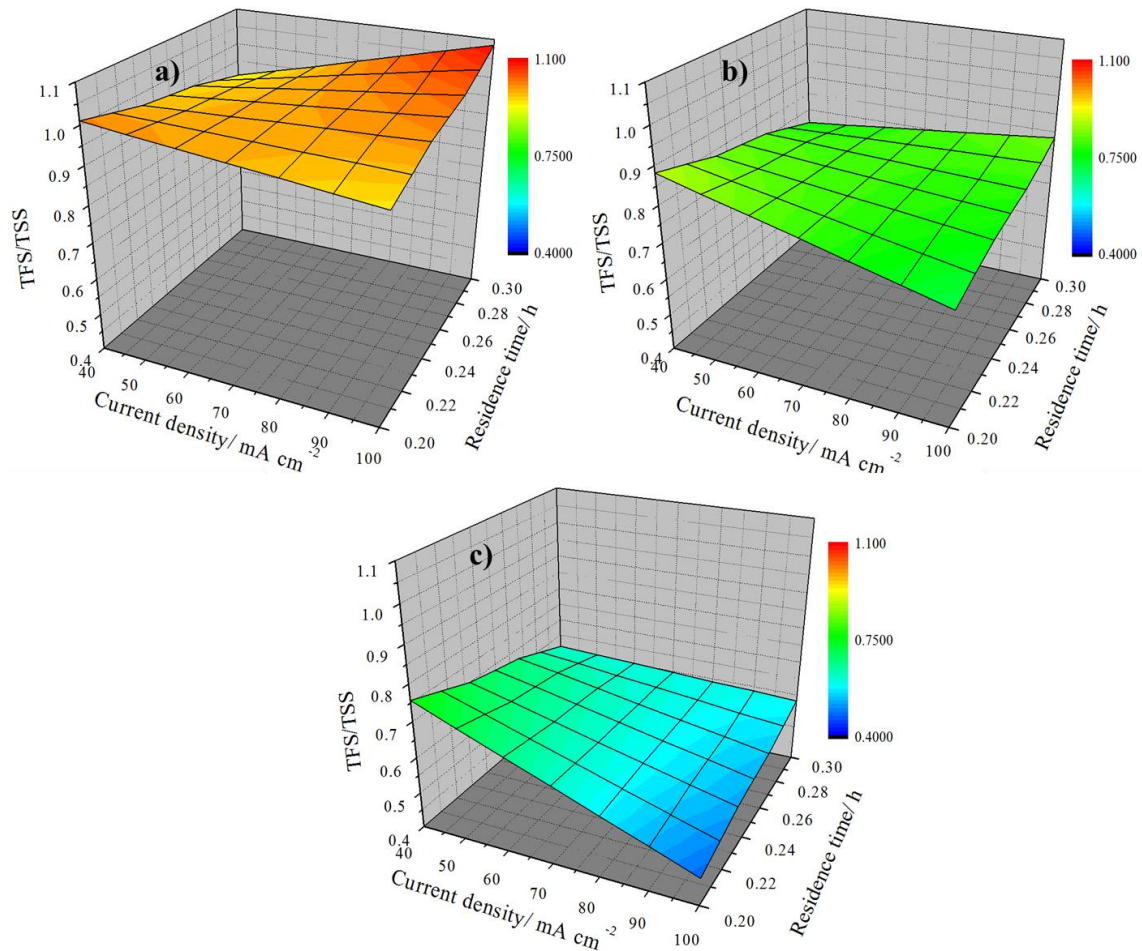


Figure 8. Response surface for the TFS/TSS relationship for 3 different values of initial kaolin concentration. a) [kaolin] 500 mg/L, b) [kaolin] 1000 mg/L, c) [kaolin] 1500 mg/L. TFS: Total Floated Solids; TSS: Total Settled Solids.

When working with kaolin as pollutant model, it can be seen that the main parameter affecting floated solids produced is initial kaolin concentration. For the lower kaolin concentration the TFS/TSS ratio is maximum and around 1. This means that for the best

conditions studied, the amount of floated solids is similar to those settled. The decrease of the TFS/TSS ratio when increasing kaolin concentration can be due to the increase of solids that favours the flocculation process, so bigger solids are formed that are more difficult to float by action of the hydrogen bubbles produced in the cathode of the reactor.

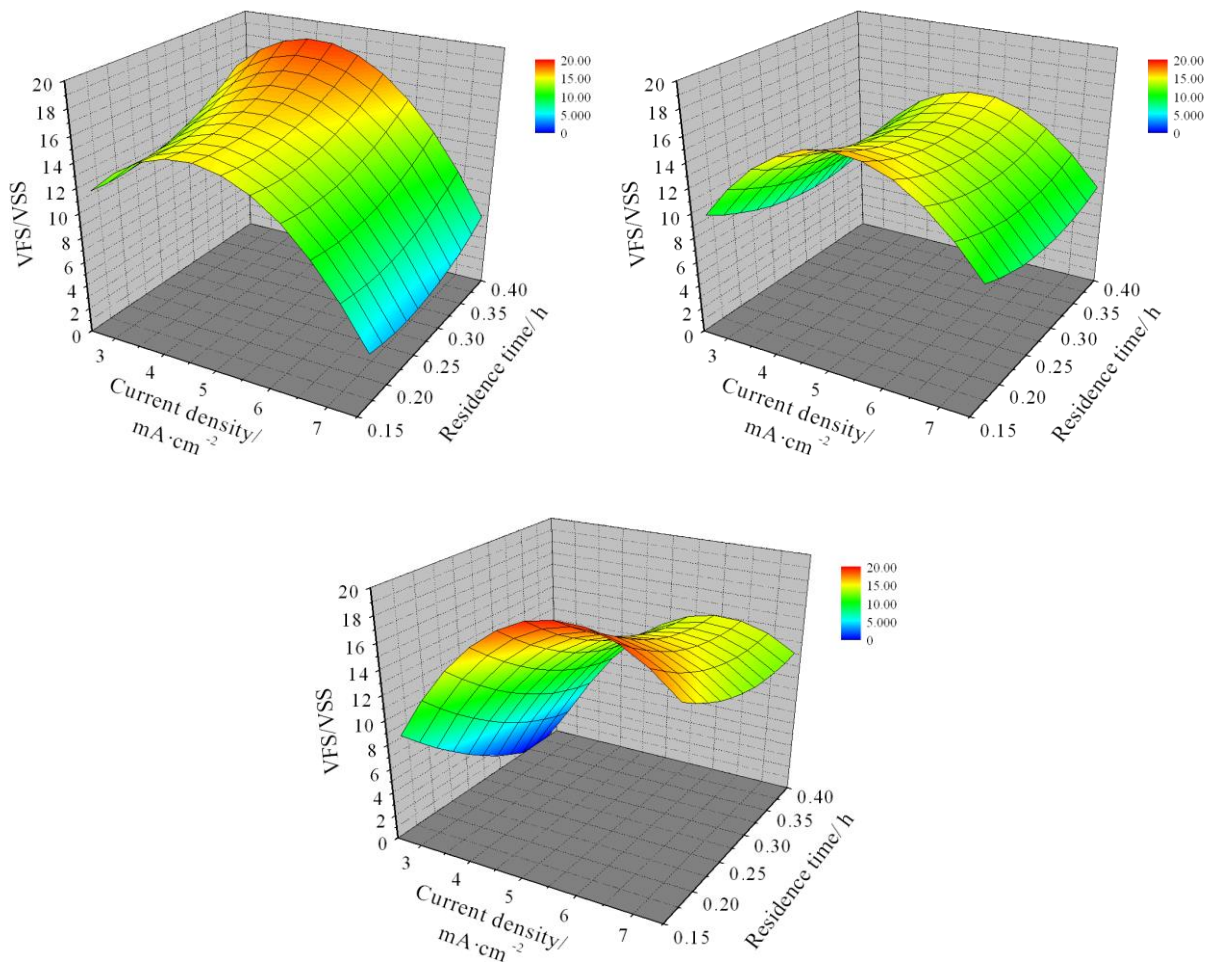


Fig. 9 Response Surface for volatile floated-settled solids ratio when using EBT as a model of pollutant. EBT concentration: a) 50 mg/L; b) 150 mg/L; c) 250 mg/L. VFS: Volatile Floated Solids; VSS: Volatile Settled Solids.

When working with EBT solutions, it can be appreciated that a maximum ratio VFS/VSS is obtained as a function of current density. This maximum can be explained taking into account

that the collision efficiency between particles and bubbles during the flotation step depends on the size of both (Ahmed & Jameson 1985). Moreover, in previous work of our group (Jimenez et al. 2010) it was observed that the size of hydrogen bubbles produced electrochemically depends on current density. It decreases with current density up to a minimum and then it increases due to coalescence processes. Furthermore, maximum floated-sedimented solids ratio is around 18. This means that floated solids concentration is up to 18 times higher than sedimented what means that the reactor is working properly in floating the flocs formed.

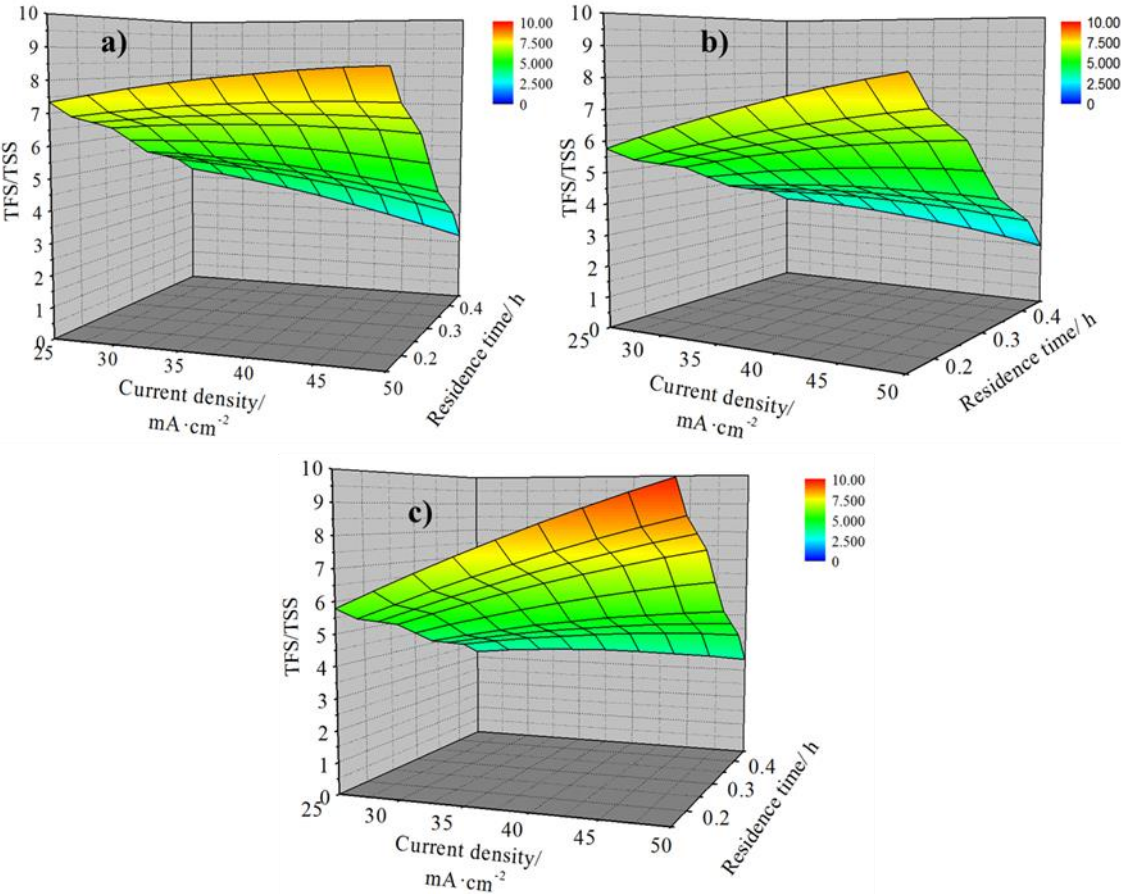


Fig. 10 Response Surface for total floated-settled solids ratio when using O/W emulsions as a model of pollutant. Oil concentration: a) 1000 mg/L; b) 3000 mg/L; c) 5000 mg/L

As it can be seen in Figure 10, TFS/TSS ratio for oil-in-water emulsions increases with current density, initial oil concentration and, especially with residence time, as the oil microbubbles are more time inside the reactor to float. Moreover, the TFS/TSS ratio is around 10, what means that floated solids are ten times higher than settled. Again, it can be seen that the combined reactor has a good efficiency in the removal of flocs.

5. Conclusions

The main conclusions of this work are:

- The combined treatment of wastewater through electrocoagulation and electroflotation techniques achieves good results in the removal of pollutants that form low density solids during the electrocoagulation stage (dyes solutions and oil-in-water emulsions). These types of solids can be easily dragged to the reactor surface by the hydrogen bubbles produced during the electroflotation process.
- During the treatment of wastewater with pollutants that form high density solids during the electrocoagulation process (colloids suspensions such as the kaolin suspension tested), the removal of the solids formed using an electroflotation process reduces the efficiency of the global process, as the solids are better separated from the coagulated dispersion by sedimentation.
- As compared to iron, the use of aluminium electrodes during the electrocoagulation leads to better results in the separation of the oil droplets formed during the treatment of oil-in-water emulsions because of the lower density of the aluminium flocs formed. During the treatment of eriochrome black T solutions, similar efficiencies are obtained with both aluminium and iron. Nevertheless, the time required for achieving a high removal of the flocs is much lower when aluminium is used as coagulant.

- The use of a combined electrocoagulation-electroflotation prototype reactor leads to good results in the separation of solids through electroflotation, especially for those pollutants that form solids of low density
- RSM allows modelling the results obtained in a combined electrocoagulation-electroflotation reactor for the removal of kaolin, EBT and oil concentration of an oil-in-water emulsion and for the floated-settled solids ratio achieved inside the reactor.

Acknowledgements

The authors acknowledge funding support from the EU and Spanish Government through the MINECO Project CTM2013-45612-R, FEDER 2007-2013 PP201010 (Planta Piloto de Estación de Estación de Regeneración de Aguas Depuradas) and INNOCAMPUS

6. References

- Ahmed N, Jameson GJ (1985): THE EFFECT OF BUBBLE-SIZE ON THE RATE OF FLOTATION OF FINE PARTICLES. *International Journal of Mineral Processing* 14, 195-215
- Bonilla CF (1947): Possibilities of electronic coagulator for water treatment. *Water sewage* 85, 44-45
- Canizares P, Martinez F, Jimenez C, Lobato J, Rodrigo MA (2006): Coagulation and electrocoagulation of wastes polluted with dyes. *Environmental Science & Technology* 40, 6418-6424
- Canizares P, Jimenez C, Martinez F, Saez C, Rodrigo MA (2007a): Study of the electrocoagulation process using aluminum and iron electrodes. *Industrial & Engineering Chemistry Research* 46, 6189-6195
- Canizares P, Martinez F, Jimenez C, Lobato J, Rodrigo MA (2007b): Coagulation and electrocoagulation of wastes polluted with colloids. *Separation Science and Technology* 42, 2157-2175
- Canizares P, Martinez F, Jimenez C, Saez C, Rodrigo MA (2008): Coagulation and electrocoagulation of oil-in-water emulsions. *Journal of Hazardous Materials* 151, 44-51
- Clesceri LSGAEEI, American Public Health A, Water Environment F, American Water Works A (1998): Standard methods for the examination of water and wastewater. American Public Health Association, Washington
- Chavalparit O, Ongwandee M (2009): Optimizing electrocoagulation process for the treatment of biodiesel wastewater using response surface methodology. *Journal of Environmental Sciences-China* 21, 1491-1496
- Chen GH (2004): Electrochemical technologies in wastewater treatment. *Separation and Purification Technology* 38, 11-41

- Essadki AH, Gourich B, Vial C, Delmas H, Bennajah M (2009): Defluoridation of drinking water by electrocoagulation/electroflotation in a stirred tank reactor with a comparative performance to an external-loop airlift reactor. *Journal of Hazardous Materials* 168, 1325-1333
- Gurses A, Yalcin M, Dogar C (2002): Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables. *Waste Management* 22, 491-499
- Holt PK, Barton GW, Wark M, Mitchell CA (2002): A quantitative comparison between chemical dosing and electrocoagulation. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 211, 233-248
- Hosny AY (1992): Separation of oil from oil/water emulsions using an electroflotation cell with insoluble electrodes. *Filtration & Separation* 29, 419-423
- Jimenez C, Talavera B, Saez C, Canizares P, Rodrigo MA (2010): Study of the production of hydrogen bubbles at low current densities for electroflotation processes. *Journal of Chemical Technology and Biotechnology* 85, 1368-1373
- Jimenez C, Saez C, Martinez F, Canizares P, Rodrigo MA (2012): Electrochemical dosing of iron and aluminum in continuous processes: A key step to explain electro-coagulation processes. *Separation and Purification Technology* 98, 102-108
- Ketkar DR, Mallikarjunan R, Venkatachalam S (1991): ELECTROFLOTATION OF QUARTZ FINES. *International Journal of Mineral Processing* 31, 127-138
- Khemis M, Leclerc JP, Tanguy G, Valentin G, Lapicque F (2006): Treatment of industrial liquid wastes by electrocoagulation: Experimental investigations and an overall interpretation model. *Chemical Engineering Science* 61, 3602-3609
- Koby M, Demirbas E, Bayramoglu M, Sensoy MT (2011): Optimization of Electrocoagulation Process for the Treatment of Metal Cutting Wastewaters with Response Surface Methodology. *Water Air and Soil Pollution* 215, 399-410
- Korbahti BK, Tanyolac A (2008): Electrochemical treatment of simulated textile wastewater with industrial components and Levafix Blue CA reactive dye: Optimization through response surface methodology. *Journal of Hazardous Materials* 151, 422-431
- Korbahti BK, Artut K, Gecgel C, Ozer A (2011): Electrochemical decolorization of textile dyes and removal of metal ions from textile dye and metal ion binary mixtures. *Chemical Engineering Journal* 173, 677-688
- Korbahti BK, Artut K (2013): Bilge Water Treatment in an Upflow Electrochemical Reactor using Pt Anode. *Separation Science and Technology* 48, 2204-2216
- Merzouk B, Madani K, Sekki A (2010): Using electrocoagulation-electroflotation technology to treat synthetic solution and textile wastewater, two case studies. *Desalination* 250, 573-577
- Mollah MYA, Schennach R, Parga JR, Cocke DL (2001): Electrocoagulation (EC) - science and applications. *Journal of Hazardous Materials* 84, 29-41
- Rajeshwar JG, Ibañez K (1997): *Environmental Electrochemistry, Fundamentals and Applications in Pollution Abatement*. Academic Press, London, UK
- Raju GB, Khangaonkar PR (1984): ELECTROFLOTATION - A CRITICAL-REVIEW. *Transactions of the Indian Institute of Metals* 37, 59-66
- Strokach PP (1975): The prospects of using anodic dissolution of metal for water purification. *Electrochemistry in industrial Processing and Biology. Electrochem. Ind. Process. Bio.* 55, 375
- Stuart EE (1946): Electronic water purification progress report on the electronic coagulator. A new device which gives promise of unusually speedy and effective results. *Water sewage* 84, 24-26
- Tir M, Moulai-Mostefa N (2008): Optimization of oil removal from oily wastewater by electrocoagulation using response surface method. *Journal of Hazardous Materials* 158, 107-115
- Zodi S, Potier O, Lapicque F, Leclerc J-P (2009): Treatment of the textile wastewaters by electrocoagulation: Effect of operating parameters on the sludge settling characteristics. *Separation and Purification Technology* 69, 29-36

- Zodi S, Potier O, Lapicque F, Leclerc J-P (2010): Treatment of the industrial wastewaters by electrocoagulation: Optimization of coupled electrochemical and sedimentation processes. *Desalination* 261, 186-190
- Zodi S, Potier O, Merzouk B, Lapicque F, Leclerc J-P (2013): Direct red 81 dye removal by a continuous flow electrocoagulation/flotation reactor. *Separation and Purification Technology* 108, 215-222
- Zongo I, Leclerc J-P, Maiga HA, Wethe J, Lapicque F (2009a): Removal of hexavalent chromium from industrial wastewater by electrocoagulation: A comprehensive comparison of aluminium and iron electrodes. *Separation and Purification Technology* 66, 159-166
- Zongo I, Maiga AH, Wethe J, Valentin G, Leclerc J-P, Paternotte G, Lapicque F (2009b): Electrocoagulation for the treatment of textile wastewaters with Al or Fe electrodes: Compared variations of COD levels, turbidity and absorbance. *Journal of Hazardous Materials* 169, 70-76