

Break-up of oil-in-water emulsions by electrochemical techniques

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Abstract

Electrochemically-assisted technologies can be successfully applied to the treatment of oil-in-water (O/W) emulsions. In this work, it is studied the influence of the main parameters (electrical charge passed, pH, electrolyte, oil content and operation mode) in the efficiency of these processes, when aluminium electrodes are used. The pH was found to be the most significant parameter, and good removal efficiencies were only obtained for pHs in the range 5–9. The electrical charge passed was observed to be directly related to the aluminium supplied to the waste. For a given oil concentration it is required that a minimum electrical charge is passed to break-up the emulsion. Further increases in the electrical charge lead to increase in the COD removal. The influence of the oil concentration is related to that of the electrical charge passed: for a given dose of aluminium, the higher the oil content the lower the COD-removal efficiency. Likewise, to produce the break-up of the emulsion it is required a minimum dose of aluminium (electrical charge passed), lower doses do not attain the rupture of the emulsion. The type of electrolyte and its concentration were also found to influence the process efficiency. Better efficiencies were obtained in the treatment of chloride-containing wastes and for low concentration of electrolyte. The destabilization of the O/W emulsion was found to be favoured in the discontinuous operation mode. Bridging flocculation is a primary destabilization mechanism that can explain the experimental results obtained in this work.

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1. Introduction

Metalworking industries generate oily wastewaters that contain stable oil-in-water emulsions. These effluents arise from the residues of emulsions that serve the purpose of lubrication, cooling, surface cleaning and corrosion prevention in the manufacturing process.

An emulsion is a dispersion of one immiscible liquid into another, through the use of a chemical reagent that reduces the interfacial tension between the two liquids to achieve stability. Commonly, this chemical reagent consists of an amphiphile molecule that contains both hydrophilic and hydrophobic groups. In case of oil-in-water (O/W) emulsions, the reagent is frequently a mineral oil. As a result of the adsorption of this reagent, the oil droplets have a net charge on their surfaces, which causes repulsion forces between them. These repulsion forces between droplets explain the stability of the emulsions. As a

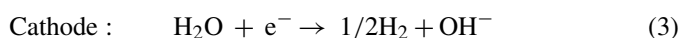
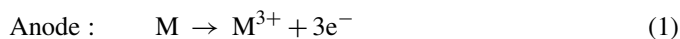
consequence of the small size of droplets in the dispersion, the macroscopic appearance of the emulsion is that of a homogenous liquid, although this mixture is really a heterogeneous system [1].

Appropriate treatment of these wastewaters is necessary in order to reduce the impact of their discharge. Different processes have been described in the literature for the treatment of these wastes, but the most commonly used are the chemical destabilization (conventional coagulation) [2–6], the electrochemical destabilization (electrocoagulation) [6–9] and the ultrafiltration [10–14]. Less expensive biological processes [15–17] are rarely used since the effluents generated in this kind of processes usually contain biocides to prevent degradation of the industrial fluids. Likewise, distillation [18] is only an attractive alternative when the effluent is highly polluted with soluble compounds that cannot be removed by other techniques, due to its high operation-cost.

The chemical and electrochemical destabilization methods involve the addition of coagulant agents to the wastewater, which promote the break down of the emulsion due to the reduction of the superficial charge of the droplets, causing the coalescence of

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the oil droplets, and the subsequent separation of the aqueous and oily phases by means of conventional settling or dissolved-air flotation. Thus, in the chemical coagulation process, it is usual the addition of a solution containing hydrolysing metal salts (of Fe^{3+} or Al^{3+}) while the electrochemical method involves the in situ generation of coagulants by electrolytic oxidation of an appropriate anode material (e.g., iron or aluminium) as it is shown in Eq. (1). In both cases, the chemistry of the hydrolyzed metal salts is complex. Moreover, in the electrochemical process, the electrodisolution of the anode competes with the oxidation of water (Eq. (2)). On the cathode, the reduction of water occurs (Eq. (3)).



Related to the differences between the conventional and the electrochemical destabilization methods, one of the advantages reported in the literature for the electrochemical treatment is the generation of bubbles (the O_2 and overall, the H_2 produced in the reduction of water) on the electrode surfaces (Eqs. (2) and (3)). These bubbles promote the coalescence process (electrofloculation) [19,20], and the separation of the coalesced droplets, which can be carried to the top of the solution, where they can be easily collected and removed (electroflotation process) [21–23]. Thus, it is reported that the combination of electrocoagulation and electroflotation techniques increases the efficiency of the process [24,25]. Some other advantages of electrocoagulation method are the simple equipment required and the easy automation of the process [25–28], as it does not require any addition of chemicals. In addition, the low requirement of current allows to be run by green energy process as solar, windmills and fuel cells [25]. Thus, the results obtained allow classifying this technique as one of the most promising methods for treating wastewater streams consisting of oil-in-water emulsions.

The goal of this paper is to study the electrochemical demulsification of an O/W emulsion using aluminium electrodes, and to try to determine the influence of the emulsion characteristics (oil concentration, pH and type and concentration and type of supporting electrolyte), as well as the operating parameters (electrical charge applied and operation mode) in the results obtained by this treatment technology.

2. Experimental

2.1. O/W emulsions

The oily phase of the emulsion is composed by a common lubricant oil (REPSOL ELITE TDI 15W40 provided by REPSOL-YPF, Spain) and a soluble oil (SOL 1000 provided by Molydal, France). To prepare the emulsion, the same amounts of both lubricant and soluble oils (50:50, w/w) were mixed and stirred until a homogenous liquid was obtained. Then, the supporting electrolyte (NaCl or Na_2SO_4) dissolved in osmotized

water was added slowly while the mixture was being stirred to finally obtain the oil-in-water emulsion.

2.2. Experimental devices

The electrocoagulation experiments have been carried out in a bench-scale plant, with a single compartment electrochemical flow cell as described in previous works [29,30]. Aluminium electrodes (HE 18) were used as anode and cathode. Both electrodes were square in shape (100 cm^2), and with an electrode gap of 9 mm. The electrical current was applied using a DC Power Supply FA-376 PROMAX. The current flowing through the cell was measured with a 2000 Digital Multimeter KEITHLEY. The electrolyte was stored in a 5000 ml glass tank stirred by an overhead stainless steel rod stirrer HEIDOLPH RZR 2041 and thermostated by means of a water bath, which allowed maintaining the temperature at the desired set point. The emulsion was circulated through the electrolytic cell by means of a peristaltic pump. The experiments were carried out under galvanostatic conditions.

2.3. Continuous operation mode experiments

In the continuous operation mode, the O/W emulsion was pumped from the feed tank to the cell and then it was collected in a different tank. Samples were taken at the outlet of the cell and left 60 min to allow the coalescence of the phases. This period was selected after some preliminary experiments. After this time, COD (using a HACH DR2000 analyser) and pH (using an inoLab WTW pH meter) were measured in the aqueous phase. Before each experiment the electrodes were treated with a solution of HCl 1.30 M in order to reject any effect due to the different prehistory of the electrodes.

2.4. Batch operation mode experiments

The discontinuous electrocoagulation experiments were carried out by recirculating the effluent of the treatment to the feed tank. Samples were taken and analyzed in the same manner than those of the continuous process.

2.5. Measurement of the aluminium dissolved in the cell

The heterogeneity of the emulsion and the formation of two phases after the coalescence, make the accurate measurement of the total aluminium dissolved in the cell difficult in every experiment, as many source of errors can be present (quantification of the phases volumes, determination of aluminium in both phases . . .). To obtain precise data, every experiment (continuous or batch) was repeated maintaining the same operation conditions and changing the O/W emulsion by an aqueous solution with the same concentration of electrolyte. Results obtained in preliminary experiments demonstrate that the concentration of aluminium is not affected by the oil content and then a simple and more accurate measurement is obtained with this procedure. Then, the concentration of aluminium was measured off-line using an inductively coupled plasma LIBERTY SEQUENTIAL

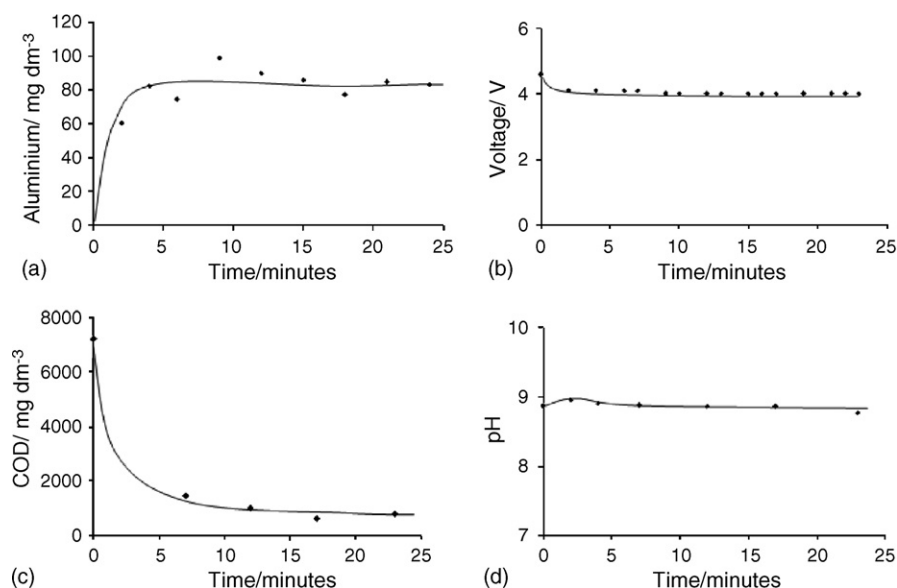


Fig. 1. Dynamic responses of aluminium concentration, cell potential, COD and pH obtained in a typical continuous electrocoagulation experiment. Temperature, 25 °C; flow rate, 10.7 dm³ h⁻¹; oil concentration, 3000 mg dm⁻³; supporting media, 3000 mg NaCl dm⁻³; current density, 16.0 mA cm⁻²; initial pH, 8.9.

VARIAN according to a standard method [31] (plasma emission spectroscopy). To determine the amount of soluble aluminium, the concentration was measured directly, while to determine the total aluminium concentration samples were diluted 50:50 (v/v) with 4 N HNO₃.

3. Results and discussion

3.1. Dynamic response of the continuous electrocoagulation process

Fig. 1 shows the changes in the main parameters during one typical continuous electrocoagulation experiment (temperature, 25 °C; flow rate, 10.7 dm³ h⁻¹; oil concentration, 3000 mg dm⁻³; supporting media, 3000 mg NaCl dm⁻³; current density, 16.0 mA cm⁻²; initial pH, 8.9). As a result of the electrode dissolution (Eq. (1)), the aluminium concentration in the treated waste increases until a constant value of approximately 80 mg dm⁻³ (Fig. 1a). The increase in the ionic strength reduces the electrolyte resistance and makes the cell potential decrease (Fig. 1b). Likewise, the presence of aluminium promotes destabilization of the emulsion and, after the coalescence process, it leads to the separation of the organic phase from the aqueous solution. Consequently, the COD of the aqueous phase (effluent of the treatment) decreases (Fig. 1c).

The pH (Fig. 1d) achieves a small maximum before attaining a constant value and the steady-state pH is slightly higher than the initial one. This is a typical dynamic response for the pH, as it can be observed in Fig. 2 that shows the changes in the pH in different electrocoagulation experiments. As it can be observed, an inverse response of pH with time (successive increase and decrease of the pH) is obtained in these experiments, being this behaviour characteristic of complex processes. To explain these strange changes in the pH, it has to be taken into account that in the cell some electrochemical and chemical processes occur

simultaneously. Thus, the cathodic reduction of H₂O (Eq. (3)) makes the pH increase, while the formation of the different aluminium species (by combination of the electrodisolved Al³⁺ ions with hydroxyl ions according to the equilibrium reactions (4)–(8)) lead to decreases in the pH. In addition, the acid–base equilibria of other species present in the waste such as carbonates (Eqs. (9) and (10)) and the autoprotolysis of water (Eq. (11)) can also influence importantly the bulk pH. All these parameters (aluminium, pH, COD, and conductivity) reach a steady-state value for times lower than ten-times the hydraulic residence time of the cell. These responses are representative of the variations observed in the parameters studied in most of the experiments.

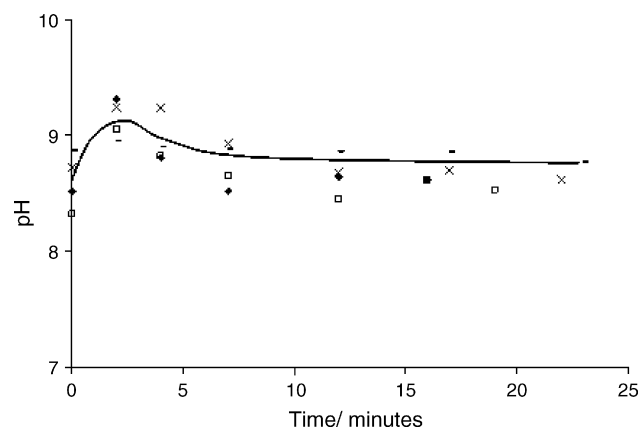
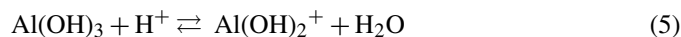
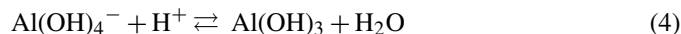


Fig. 2. Dynamic responses of pH obtained in (four) continuous electrocoagulation experiments. Temperature, 25 °C; oil concentration, 3000 mg dm⁻³; supporting media, 3000 mg NaCl dm⁻³; electrical charge passed, (♦) 0.0935 A h dm⁻³; (□) 0.2041 A h dm⁻³; (○) 0.1495 A h dm⁻³; (×) 0.2653 A h dm⁻³.

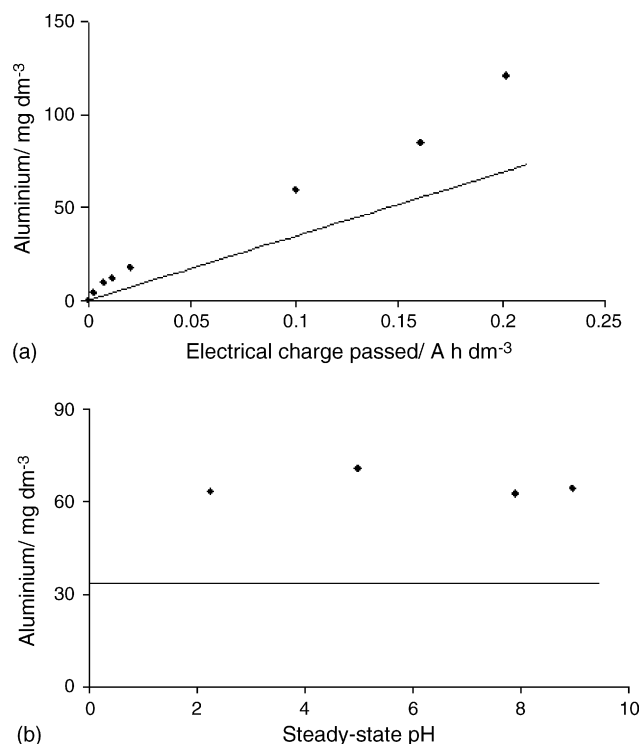
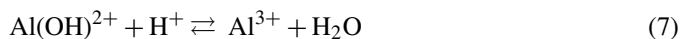
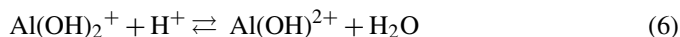


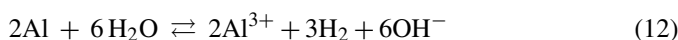
Fig. 3. Concentration of aluminium generated in continuous electrochemically-assisted coagulation process as a function of the electrical charge passed and the pH. Temperature, 25 °C; supporting media, 3000 mg NaCl dm⁻³. (a) (—) Faraday's Law; (◆) experimental values. (b) Electrical charge passed, 0.10 A h dm⁻³; (—) Faraday's Law; (◆) experimental values.



The amount of aluminium generated in the experiment exceeds the value calculated if the process is considered to be only electrochemical (if it is considered that aluminium can only come from anodic oxidation of the aluminium sheet at the current intensity maintained in the cell). This fact is also observed in all the experiments carried out in this work. Thus, Fig. 3 shows the amount of aluminium generated in the electrocoagulation process as a function of the electrical charge passed and of the pH. This figure also shows, for comparison purposes, the theoretical values corresponding to the amount of aluminium generated assuming the process is purely electrochemical. It can be seen that in all cases the amounts of aluminium dissolved are over the theoretical values, although this behaviour is more marked for lower electrical charges passed. It can also be seen that the amount of aluminium generated is almost constant with the steady-state pH in the range studied.

These super-faradaic efficiencies are reported in literature [32,33], and they can be explained in terms of the chemical

dissolution of the aluminium sheets. Thus, the chemical dissolution process (Eq. (12)) has been previously characterized by our group [32], and in these early studies it was found that this process depends mainly on the pH in the nearness of the aluminium sheets, and that the chemical dissolution rate of aluminium is several orders of magnitude higher at alkaline pHs. In this study, it was also shown that electrochemical oxidation and reduction of H₂O (Eqs. (2) and (3)) generates a pH profile between anode and cathode. On the anode, the water oxidation process (oxygen evolution) generates a high concentration of protons and this leads to a local acidic pH. On the cathode, the water reduction process results in the formation of hydroxyl ions and consequently in a local alkaline pH in the proximities of the cathode surface. This higher pH increases significantly the aluminium chemical dissolution rate and consequently, it explains the higher concentration of dissolved aluminium.



In this case, the large potentials required to produce the high concentration of aluminium (as compared to those required in the electrocoagulation of dissolved organic matter [30] or colloids [29]) produce simultaneously huge amounts of hydroxyl ions (as a consequence of the water reduction process that occurs in the cathode shown in Eq. (3)). These large amounts of hydroxyl ions and the segregated flow cell that can be considered to take place in the flow electrochemical cell [32] achieve that the pH in the proximity of the cathode will be very alkaline independently of the bulk pH. This can explain the constant contribution of the chemical dissolution process to the dissolution of aluminium (Fig. 3b).

3.2. Influence of operation parameters in the continuous electrocoagulation process

Fig. 4 shows the influence of the pH on the electrodestabilization process, where the electrical charge passed is similar (and so the concentration of dissolved aluminium). Abrupt changes are observed in the obtained results. Experiments in which the steady-state pH is out of the range 5–9 produce no emulsion break-up and consequently no removal of COD. Inside this

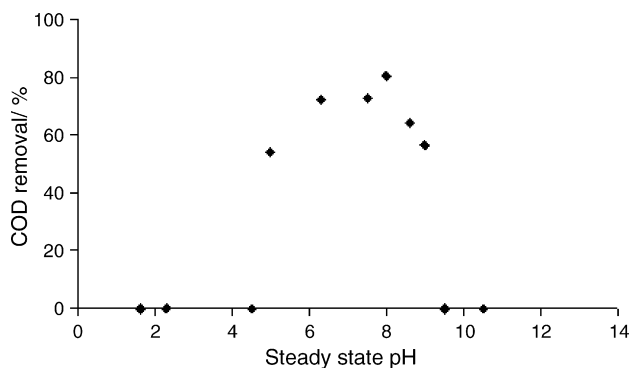


Fig. 4. Influence of the pH in the removal of COD in the continuous electrocoagulation process. Temperature, 25 °C; flow rate, 10.7 dm³ h⁻¹; oil concentration, 3000 mg dm⁻³; supporting media, 3000 mg NaCl dm⁻³; current density, 10.5 mA cm⁻².

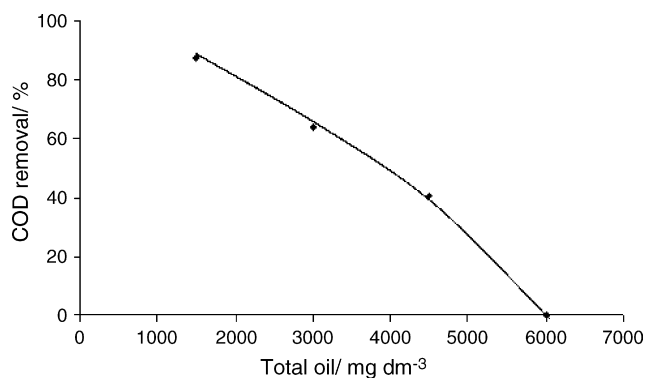


Fig. 5. Influence of the total oil concentration in the COD removal achieved in the continuous electrocoagulation experiments. Temperature, 25 °C; flow rate, 10.7 dm³ h⁻¹; current density, 10.5 mA cm⁻²; initial pH, 8.5; supporting media, 3000 mg NaCl dm⁻³.

range, the obtained removals of COD vary between 60 and 80%. According to the literature [34–37], the predominant species for these conditions are polymeric hydroxoaluminium cations (specially the tridecamer) and the amorphous aluminium hydroxide precipitate. The surface of this later species can be positively or negatively charged by the adsorption of ions from the solution. On the contrary, outside the range of pH, which promotes the destabilization, the primary aluminium species are monomeric-hydroxoaluminium ions. These include cations such as Al³⁺, Al(OH)²⁺, Al(OH)₂⁺ in the acidic range and anions such as Al(OH)₄⁻ in the alkaline range.

Although the droplets are charged and the attachment of more than one droplet at a time to a charged destabilization-reagent (bridging flocculation) should be the primary destabilization mechanism, it is clear that this is not promoted by monomeric species and consequently only polymeric hydroxoaluminium cations or charged aluminium hydroxide precipitates can promote the emulsion break-up. This is important, because due to steric constraints (its small size as compared to the size of a droplet) every monomeric aluminium ionic species can only act over a given droplet. On the contrary, the size of the polymeric ions, and specially that of the precipitate, can achieve that more than one droplet can be associated to one of this coagulant species. In this case, the organics content in the linked droplets can be placed close enough to promote the coalescence.

Fig. 5 shows the influence of the total amount of oil contained in the emulsion (for a given concentration of aluminium electrodisolved). It can be observed that the higher the concentration of oil, the lower the removal of COD. This fact shows that the amount of aluminium necessary to produce the break-up of the emulsion is proportional to the concentration of oil emulsified. Other important point to be considered is that for a given dose of aluminium there is a limit concentration of oil in the emulsion that allows the treatment. For higher concentration of oil in the emulsion not rupture is obtained at the operation conditions shown in Fig. 5.

The influence of the electrical charge passed in the continuous electrocoagulation process is shown in Fig. 6. It can be observed that for the oil concentration selected (3000 mg dm⁻³), the de-emulsification only occurs for values of the electrical charge

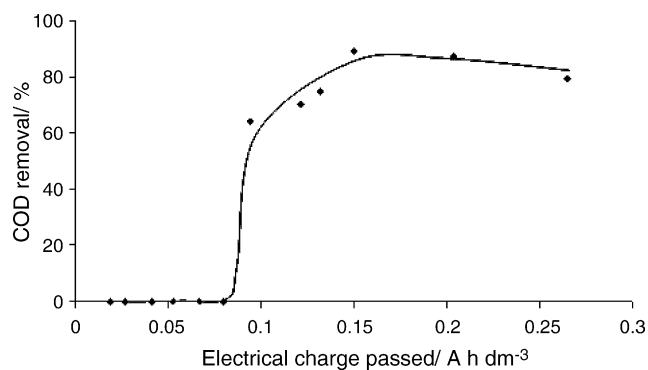


Fig. 6. Steady-state of COD removal achieved in the continuous electrocoagulation experiments as a function of the electrical charge passed. Temperature, 25 °C; oil concentration, 3000 mg dm⁻³; supporting media, 3000 mg NaCl dm⁻³; initial pH, 8.5.

higher than 0.1 A h dm⁻³ (an abrupt change is observed at this point), and from this value the removal of COD increases to achieve a maximum at 0.14 A h dm⁻³. From this value additional charges lead to small decrease in the efficiency of the COD removal. This indicates that excess in the concentration of coagulant can reduce the efficiency. This increase may either correspond to an increase in the number of charged-aluminium-hydroxide particles and thus, to a decrease in the possibility of that more than one droplet of oil is connected to the same particle (which is the first stage needed to promote the coalescence of the oil droplets) or more likely to an increase in the average size in the particles, and thus, to a less efficient use of the aluminium (less surface of particles per mass unit of aluminium dissolved).

Fig. 7 shows the results obtained in the continuous electrocoagulation process as a function of the concentration of electrolyte (NaCl). The lower the concentration of salt the higher is the COD removal. Likewise, for NaCl concentrations over 3000 mg dm⁻³ the process yield the same removal of oil (nearly 70% for the dose of aluminium added). To study the influence of the type of electrolyte on the system, several experiments with Na₂SO₄ as electrolyte were carried out. Fig. 8 shows the changes of COD removal with the electrical charge passed for both electrolytes studied. It can be seen that in sulphate medium the electrical

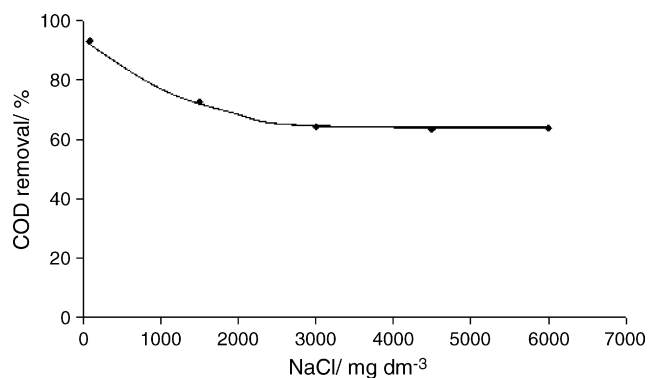


Fig. 7. Influence of the concentration of salt in the continuous electrocoagulation experiments. Supporting media, NaCl; temperature, 25 °C; flow rate, 10.7 dm³ h⁻¹; current density, 10.5 mA cm⁻²; initial pH, 8.5; oil concentration, 3000 mg dm⁻³.

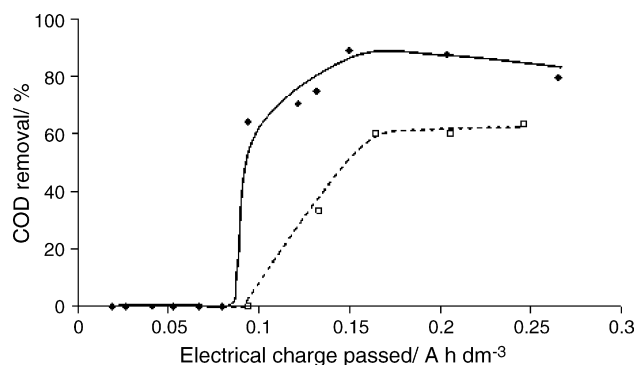


Fig. 8. Influence of the supporting electrolyte in the continuous electrocoagulation experiments. Temperature, 25 °C; oil concentration, 3000 mg dm⁻³; initial pH, 8.5; supporting media, (◆) 3000 mg NaCl dm⁻³, (□) 3000 mg Na₂SO₄ dm⁻³.

charge passed necessary to achieve the break-up of the emulsion is larger than in chloride medium. Likewise, for the same electrical charge passed, better removals of COD are obtained in chloride medium. Moreover, it can be observed that in case of sulphate-containing emulsions, there is no optimum dosage of aluminium, as the COD removal achieves a constant value with the electrical charge passed.

Both observations (the effect of the concentration of chlorides and the effect of the type of the electrolyte) can be explained in terms of the formation of aluminium species, which is largely influenced by the presence of these ions. Thus, it is reported that sulphate media promotes the formation of precipitates over the formation of polymeric hydroxo-ions. This can be clearly observed in Table 1, which summarizes the percentages of soluble aluminium in both media for different current charges. These percentages do not seem to depend importantly on the total concentration of aluminium (according to Fig. 3 the concentration of aluminium is directly related to the specific current charge passed), although a slight increase is observed with the charge passed. However, the influence of the media is clear: in the sulphate media the 70% of the aluminium is in the form of amorphous aluminium hydroxide precipitate and in the chloride media this percentage is around 40%. According to the literature [34–37], the remaining aluminium should be mainly in the form of polymeric hydroxocations. This means that the active sites that promotes the coalescence are higher in the chloride media (the aluminium is more efficiently used) as the aluminium

Table 1
Percentage of soluble aluminium generated in the electrochemically-assisted coagulation process as a function of the supporting electrolyte and the electrical charge passed

Electrical charge passed (Ah dm ⁻³)	Soluble aluminium (%)	
	NaCl	Na ₂ SO ₄
0.09	54.6	32.7
0.13	55.3	32.8
0.15	55.6	32.8
0.20	56.0	32.9

Temperature, 25 °C; initial pH, 8.5; supporting media, 3000 mg NaCl dm⁻³ and 3000 mg Na₂SO₄ dm⁻³.

hydroxide which is not on the surface of the particles is not effective from the treatment point of view, and due to its smaller size (and thus, to their more efficient aluminium content) the polymeric ions are expected to yield better efficiencies.

Other point that explains the previous experiments, is the adsorption of chloride or sulphate ions onto the surface of the aluminium hydroxide precipitates. This adsorption can reduce the net positive charges of the surfaces of the particles (in the acidic range) or increase the negatively charged sites (in the alkaline range). The effect is more important with the sulphate ion due to its higher charge. Consequently, this can also explain the different results obtained.

To study the influence of the operation mode, several experiments in batch operation mode were carried out. Fig. 9 shows the comparison between the continuous and batch electrocoagulation of oil-in-water emulsion as a function of the aluminium concentration generated in the processes. As it can be seen, similar removals are yielded by both processes at high concentrations of aluminium, while in the batch process a lower concentration of aluminium is enough to attain the coalescence of the phases. Conversely, the changes in the pH are similar in both processes.

To explain the differences between both operation modes, it has to be considered that the addition of aluminium in the continuous process is instantaneous (the wastewater only pass through the cell once) and in the batch process is progressive (the wastewater is continuously recycled into the cell and the concentration of aluminium increases continuously with time during an experiment). This means that for a given dose of aluminium,

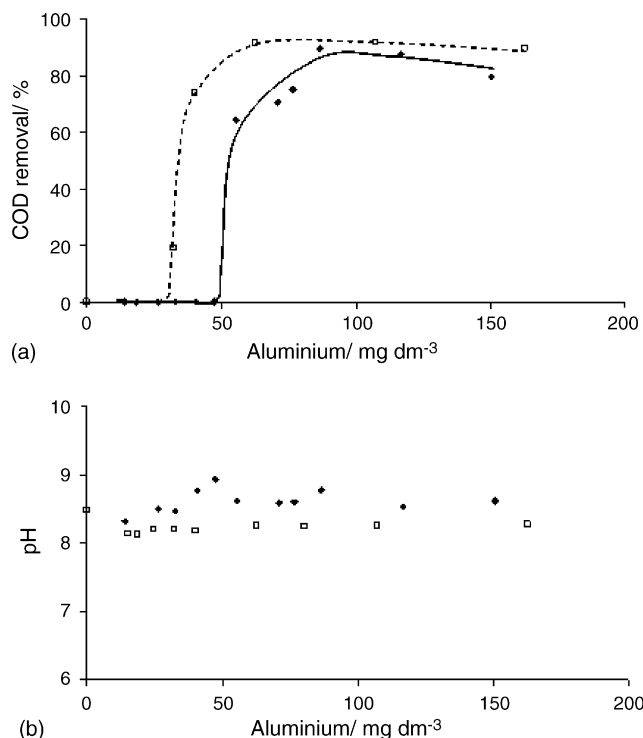


Fig. 9. Comparison between the continuous and discontinuous electrocoagulation processes. Temperature, 25 °C; initial pH, 8.5; supporting media, 3000 mg NaCl dm⁻³; oil concentration, 3000 mg dm⁻³; (◆) continuous process; (□) discontinuous process; flow rate, 19 dm³ h⁻¹; current density, 2.2 mA cm⁻²; volume, 2 dm³; time, 60 min.

the formed aluminium species can be different [38], as in the batch process the aluminium species formed can react with the oil previous to further additions of aluminium (in the following pass of the waste through the cell) and in the continuous process a given body of waste receives abruptly all its corresponding aluminium. Thus, in the later case there is a higher free aluminium concentration in the moment of addition and thus, the aluminium produced can form bigger particles of charged aluminium hydroxide precipitates (the aluminium enmeshed inside the particle is not effective) and the formation of polymeric species is not favoured. On the contrary, the batch process is going to promote more particles (and so a higher charged surface) and also more polymeric hydroxocationic species. This means that the aluminium is more efficiently used in the batch process.

4. Conclusions

From this work the following conclusions can be drawn:

1. The electrochemical destabilization process can be successfully applied in the treatment of wastes consisting of oil-in-water emulsions. The more important variables in the process are the aluminium supplied and the bulk pH. Experiments in which the steady-state pH is out of the range 5–9 produce no emulsion break-up and consequently no removal of COD. The electrolyte has also a strong influence in the obtained results.
2. The attachment of more than one droplet at a time to a charged destabilization-reagent and the subsequent coalescence is a primary destabilization mechanism that can explain the experimental results obtained in this work. This mechanism is promoted by polymeric hydroxoaluminium cations and especially by charged aluminium hydroxide precipitates and it is consistent with the observed decreases in the efficiency with the increase in the total oil concentration and with the decrease in the specific electrical charge passed, as both supports the existence of a stoichiometric ratio between the pollutant and the coagulant reagent.
3. The destabilization of the O/W emulsion is favoured in the discontinuous operation mode due to the more progressive addition of coagulant that promotes the formation of smaller particles of charged aluminium hydroxide precipitates (the aluminium enmeshed inside the particle is assumed to be not effective) and the formation of polymeric ionic species.

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