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Coagulation and electrocoagulation of oil-in-water emulsions

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Abstract

In this work the efficiencies of the chemical and the electrochemical break-up of oil-in-water (O/W) emulsions with hydrolyzing aluminium salts are compared. It has been obtained that the efficiency of the processes does not depend directly on the dosing technology, but on the total concentration of aluminium and pH. This latter parameter changes in a different way in the chemical and the electrochemical processes: the pH increases during the electrochemical experiments since the electrochemical system leads to the formation of aluminum hydroxide as a net final product, but it decreases in the conventional ones due to the acid properties of the aluminum salts added ($AlCl_3$ or $Al_2(SO_4)_3$). The break-up of the emulsions only takes place in the range of pHs between 5 and 9, and the amount of aluminium necessary to produce the destabilization of the emulsion is proportional to the oil concentration. Electrolytes containing chlorides improve COD removal as compared with those containing sulphate ions. Aluminium hydroxide precipitates were found to be the primary species present in solution in the conditions in which the breaking process is favoured. Consequently, the attachment of more than one droplet of oil at a time to a charged precipitate-particle (bridging flocculation) was proposed as the primary destabilization mechanism.
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1. Introduction

Oil-in-water (O/W) emulsions are widely used in metal industry processing, since these fluids provide the combination of cooling and lubrication required by numerous metalworking operations. These emulsions become exhausted with use as they loose their properties, and turn into residues that must be treated to reduce the impact of their discharge. The treatment of theses wastes has been addressed by different techniques, but the most commonly used are membrane processes (microfiltration and ultrafiltration) [1,2], chemical destabilization (conventional coagulation) [3–6] and electrochemical destabilization (electrocoagulation) [7–11]. Less commonly used are the biological processes, as these kinds of industrial fluids contain biocides (such as heterocyclic sulphur and nitrogen compounds) to prevent their degradation [12]. As well, when the effluent is highly polluted with soluble compounds and they cannot be removed by

other techniques, distillation [13] can be an attractive alternative, despite of its high operation-cost.

In the chemical destabilization process, it is usual the addition of hydrolyzing metal salts (of Fe^{3+} or Al^{3+}) as coagulant reagents, whereas the electrochemical method involves the in situ generation of coagulants by electrolytic oxidation of an appropriate anode material (e.g. iron or aluminium). These coagulants promote the break-up of the emulsion due to the reduction of the superficial charge of the droplets, causing the coalescence of the oil droplets, and the subsequent separation of the aqueous and oily phases by means of conventional settling or dissolved-air flotation. According to literature [14], the main destabilization mechanism is the attachment of adsorbing macromolecules to more than one droplet at a time (bridging flocculation). Destabilization by non-adsorbing polymers can also be promoted through the mechanism of depletion flocculation (that cause a weak attraction between the oil droplets). The first mechanism normally involves electrically-charged species as reagent, as these species can combine (by attractive electrical forces) with the opposite electrically-charged active sites that are present on the surface of the droplet. In addition to adsorbing

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macromolecules causing the bridging flocculation, some authors have reported the elimination of oil from emulsified effluents by the adsorption properties of growing metal hydroxides (iron and aluminium hydroxides) [10,11], which form nucleuses of particles. Around these nucleuses, adsorption layers of cations and anions are organized. The nucleus together with the adsorption layer form a particle (of metal hydroxide), which has a small positive charge, and has very high ability for adsorption of oil droplets [10].

The break-up of emulsions by solution dosing has been widely discussed in literature. However, the comparison of the mechanisms of this process and those that happens during the electrochemical dosing process is less studied. In this context, some advantages are reported in the literature for the electrochemical technique, such as the generation of bubbles (the H_2 produced in the reduction of water) on the cathode surface. These bubbles generate a soft mix in the system that promotes the coalescence process (electroflocculation) [15], 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) [16,17].

The goal of this work is to compare the efficiencies of the chemical and the electrochemical break-up of O/W emulsions with hydrolyzing aluminium salts, and to determine the similarities or differences that exist between both destabilization processes. To meet this objective, the experiments were planned to meet similar conditions between both technologies, especially in terms of aluminium dose and pH. The results have been interpreted in terms of the mechanisms previously proposed in the literature for understanding the O/W emulsions breaking process.

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. The total amount of oil added to the emulsion was in the range 1500–6000 mg dm^{-3} (0.15–0.6% of oil in the emulsion).

2.2. Experimental devices

The coagulation experiments were carried out in a bench-scale plant (described elsewhere [18]). In the electrochemical experiments, the coagulant reagent came from the dissolution of aluminium electrodes (type HE 18) placed in a single compartment electrochemical flow cell. Both electrodes (anode and cathode) were square in shape (10 cm side) and the electrode gap was 9 mm. The electrical current was applied using a DC Power

Supply FA-376 PROMAX. The voltage and the current flowing through the cell were measured with a multimeter (KEITHLEY 2000 Digital Multimeter). The O/W emulsion was stored in a 5000 cm^3 glass tank, stirred by an overhead stainless steel rod stirrer (HEIDOLPH RZR 2041) and circulated through the electrolytic cell by a peristaltic pump. A thermostated-bath allows maintaining the temperature at the desired set point. To carry out the chemical coagulation experiments the experimental bench-scale plant was modified by changing the electrochemical flow cell by a single flow reactor (with the same geometry) and by including an aluminium-solution (of $AlCl_3$ or $Al_2(SO_4)_3$) dosage system.

2.3. Experimental procedure

Electrochemical coagulation experiments were carried out under galvanostatic conditions. Prior to every experiment the electrodes were treated by rinsing with a solution of 1.30 M HCl in order to reject any effect due to the different prehistory of the electrodes.

In the continuous operation mode, the O/W emulsion was pumped from the feed tank to the cell (or reactor) 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, zeta potential (using a Zetasizer Nano ZS (Malvern, UK)), COD (using a HACH DR2000 analyser) and pH (using an inoLab WTW pH meter) were measured to the aqueous phase. Chemical coagulation experiments followed the same procedure. However, in this case the aluminium was added by dosing a solution containing $AlCl_3$ or $Al_2(SO_4)_3$.

Several discontinuous chemical experiments were carried out by recirculating the effluent from the reactor to the feed tank. In addition, some discontinuous chemical coagulation experiments were carried out in a standard jar test experimental set-up. In these later experiments, a fixed amount of coagulant was added to the emulsion, and after that the solution was vigorously stirred. The procedures to take and measure the samples were the same used for the continuous coagulation experiments.

2.4. Measurement of the aluminium electrodissolved in the cell

The heterogeneity of the emulsion and the formation of two phases after the coalescence make difficult the accurate measurement of the total aluminium electrodissolved in the cell 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 electrochemical experiment 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 oils 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

VARIAN according to a standard method [19] (plasma emission spectroscopy). To determine the total aluminium concentration, samples were diluted 50:50 (v/v) with 4N HNO$_3$ to ensure the total solubility of aluminium. A complete characterization of this electrodissolution process is shown in Supplementary data.

2.5. Characterization of the hydrolysis aluminium species generated in the chemical aluminium dosing

To characterize the hydrolysis species resulting from the addition of aluminium in the coagulation processes, several batch experiments were carried out. In these experiments, a fixed amount of coagulant-solution (AlCl$_3$ or Al$_2$(SO$_4$)$_3$) was added to an aqueous solution (NaCl or Na$_2$SO$_4$, that represents the O/W emulsion in a coagulation process), and after that the solution was stirred vigorously. Next, samples were taken and pH, zeta potential and total and soluble aluminium concentrations (by filtering the samples using membranes of 0.45 μm) were measured. In addition, the characterization of the hydrolyzed aluminium species generated has been carried out by ferron method [20–23]. This method consists of the timed spectroscopy monitoring of aluminium-ferron (8-hydroxy-7-iodo-5-quinolinesulfonic acid) reaction, to form a complex which has a maximum absorbance of 364 nm. Monomeric species react almost instantaneously with ferron, whereas polymeric species have a much slower reaction rate with this compound. The particles of precipitate practically do not react with ferron. Therefore, this method allows distinguishing among monomeric, polymeric or precipitate species.

The analytical measurement was carried out by filtering the samples using membranes of 0.45 μm in order to remove the particles of precipitate. Once the sample is filtered, an aliquot is added to a volume of saturated ferron solution freshly prepared so that ferron is in excess, at pH 5 in an acetate buffered solution. Immediately, the absorbance of the sample is monitored with time, until a constant value is obtained, what is indicative of the end of the reaction. By plotting the logarithm of the unreacted aluminium versus time, the ratio of aluminium species that react quickly and slowly with ferron (that is, monomeric and polymeric species) can be estimated [20,22,23]. A complete characterization of these species for the conditions used in this work is shown in Supplementary data.

3. Results and discussion

3.1. Dynamic response of the continuous break-up processes

In any chemical process, to characterize the behaviour of a continuous system, both the dynamic response (changes in parameters from the start-up to the steady-state) and the steady-state behaviour have to be studied. In this context, to compare the dynamic responses of the chemical and the electrochemical continuous break-up processes, some experiments were planned in order to attain similar steady-state concentration of aluminium and pH values. As it will be shown behind, the changes in the pH are different in the chemical and the electrochemical exper-

iments. Thus, to achieve similar pH values in the steady state, the initial pH of the O/W emulsions in the chemical and the electrochemical experiments had to be different.

Figs. 1 and 2 show the typical dynamic responses for the aluminium concentration, pH, COD and zeta potential (for both chemical and electrochemical coagulation processes). It can be observed that the electrochemical process needs a larger time to achieve the steady state aluminium concentration. As well, in Fig. 1b it can be observed an inverse response of pH with time (successive increase and decrease of the pH) during the electrochemical experiment, being this behaviour characteristic of complex processes. Thus, in the electrochemical process, the cathodic reduction of H$_2$O makes the pH increase, whereas the formation of the different aluminium species by combination of the electrodissolved Al^{+3} ions with hydroxyl ions according to the equilibrium reactions [23], and the oxidation of water on the anode lead to decreases in the pH. On the contrary, the pH decreases in the chemical process due to the acidic properties of the AlCl$_3$, as the aluminium added to the system is combined with hydroxyl ions according to the aluminium species equilibrium reactions [23], producing decreases in the pH.

Fig. 2a shows the changes in the zeta potential with time during the chemical and the electrochemical coagulation experiments. It can be observed that similar responses are obtained by both techniques: the initial values of zeta potential are negative (around −60 mV), and the addition of aluminium leads to the increase of this parameter to attain values around zero in the steady-state. Finally, in Fig. 2b it can be observed that
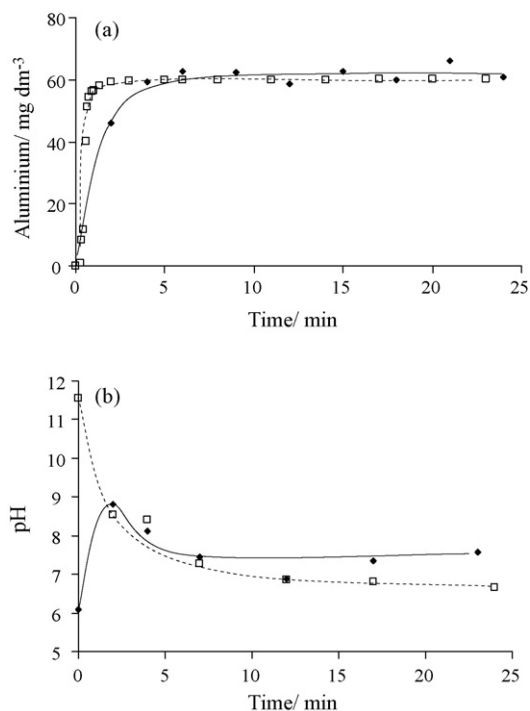

Fig. 1. Dynamic responses of aluminium concentration and pH obtained in typical continuous chemical and electrochemical coagulation processes. Temperature: 25 °C; oil concentration: 3000 mg dm^{-3}; supporting media: 3000 mg NaCl dm^{-3}. (♦) Electrochemical experiment, current density: 10.1 mA cm^{-2}; initial pH 6.0. (□) Chemical experiment, initial pH 11.5.
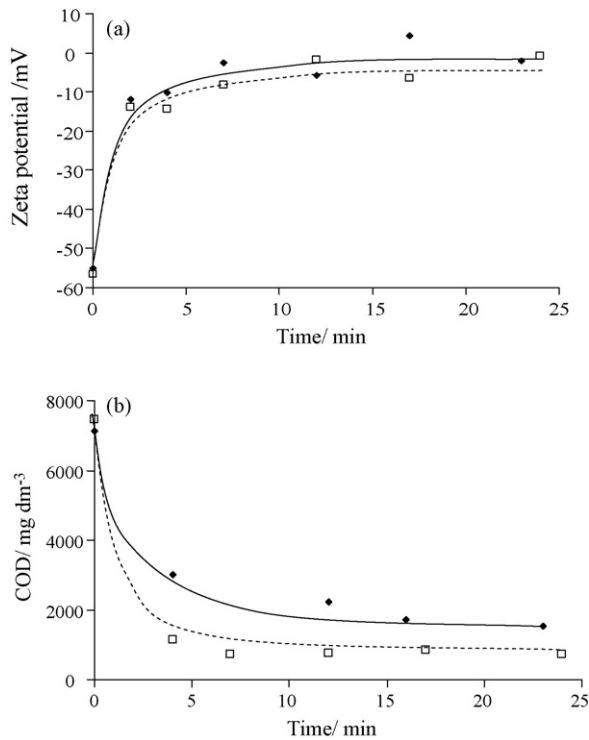
Fig. 2. Dynamic responses of (a) Zeta potential and (b) COD, obtained in typical continuous chemical and electrochemical coagulation processes. Temperature: 25 °C; oil concentration: 3000 mg dm^{-3}; supporting media: 3000 mg NaCl dm^{-3}. (♦) Electrochemical experiment, current density: 10.1 mA cm^{-2}; initial pH 6.0. (□) Chemical experiment, initial pH 11.5.

both processes are able to decrease the COD of the waste, due to the addition of the aluminium that produces the destabilization of the emulsion. As well, it can be seen that both processes achieve similar percentage removals, being slightly higher those obtained in the chemical process.

3.2. Influence of operation parameters on the continuous coagulation processes

In Fig. 3, it is shown the influence of the steady-state pH on the results obtained by conventional and electrochemical destabilization experiments. It can be observed that similar results are obtained by the chemical and the electrochemical technologies. In addition, it can be seen that the steady-state pH has a strong influence on the COD removal, as the destabilization of the emulsion is only attained for pHs in the range 5–9.

According to the aluminium speciation described in a previous work [23], it can be assumed that the aluminium species present in an aqueous solution do not depend directly on the dosing technology but on the total concentration of aluminium and pH. In this context, it is important to take into account that the aqueous chemistry of aluminium is especially complex, as it involves the formation of monomeric and polymeric hydroxoaluminium ions, and aluminium hydroxide precipitates. Thus, in the acidic range of pHs the primary species are the monomeric cationic hydroxoaluminium species. Increases in the pH lead to the coexistence of these monomeric species with increas-

ing amounts of polymeric cations and precipitates. Under pHs close to neutrality the predominant species are the aluminium hydroxide precipitates, that can be positively charged (due to the adsorption of cations from the solution), however, increases in the pH produce the charge reversal, leading to precipitates negatively charged (due to the adsorption of anions from the solution). Further increases in the pH lead to the dissolution of the precipitates to form monomeric anionic hydroxoaluminium, that is the primary species at alkaline pHs.

Fig. 4 shows the aluminium speciation in the range of pHs in which it is attained the break-up of the emulsion, and it can be seen that the predominant species for these pH conditions are the amorphous aluminium hydroxide precipitates (Fig. 4a). The surface of this species can be positively or negatively charged by the adsorption of ions from the solution, as it can be guessed from the values of the zeta potential (Fig. 4b). Contrary to values shown in Fig. 3b, the values shown in Fig. 4b were obtained in the absence of oil and stands only for the surface of the aluminium hydroxide precipitates.

Taking into account the aluminium speciation, only charged aluminium hydroxide precipitates can promote the emulsion break-up. Then, it seems clear that the attachment of more than one droplet of oil (at a time) to a charged precipitate-particle (bridging flocculation) should be the primary destabilization mechanism. In this case, the organics content in the linked droplets can be placed close enough to promote the coalescence of the oily phase [24].
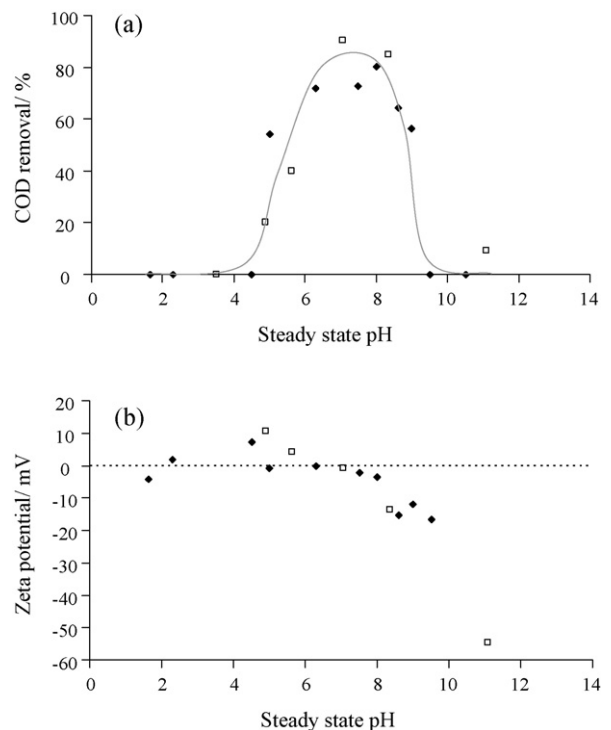

Fig. 3. Influence of the steady-state pH on the continuous chemical and electrochemical coagulation. Temperature: 25 °C; supporting media: 3000 mg NaCl dm^{-3}; oil concentration: 3000 mg dm^{-3}. (♦) Electrochemical experiments, current density: 10.1 mA cm^{-2}, (□) chemical experiments. (a) COD removal and (b) Zeta potential.
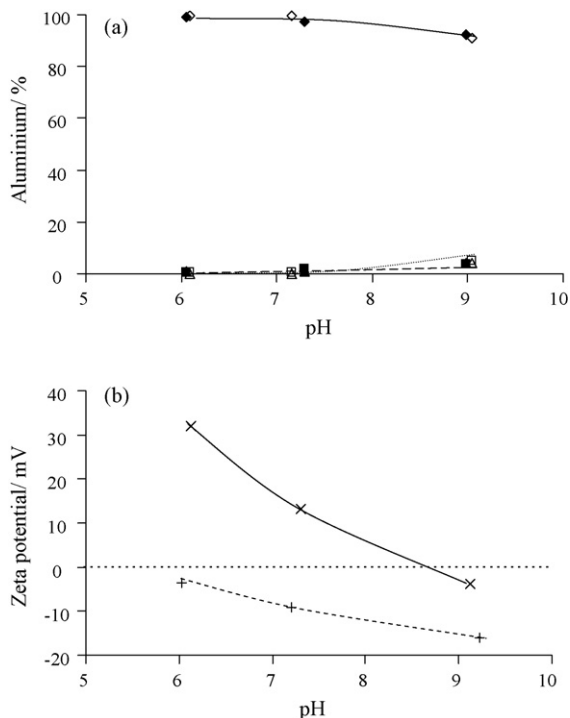
Fig. 4. Speciation of aluminium as a function of the pH, and values of zeta potential. (a) Aluminium species (expressed as % of the total aluminium concentration). Supporting media: $3000\ mg\ NaCl\ dm^{-3}$, (■) monomeric hydroxo-aluminium ions, (▲) polymeric hydroxo-aluminium ions, (♦) aluminium hydroxide precipitates. Supporting media: $3000\ Na_2SO_4\ mg\ dm^{-3}$, (□) monomeric hydroxo-aluminium ions, (△) polymeric hydroxo-aluminium ions, (◇) aluminium hydroxide precipitates. (b) Zeta potential values, supporting media: ×$3000\ mg\ NaCl\ dm^{-3}$, +$3000\ Na_2SO_4\ mg\ dm^{-3}$.

Regarding to the zeta potential values measured in the steady-state (Fig. 3b), acidic to neutral pHs lead to values near 0 mV, whereas at higher pHs, the zeta potential decreases with the increase in the pH. It is important to bear in mind that this values stands for the whole oil droplets/precipitate particles system. Then, this behaviour can be explained in terms of the charge reversal of the aluminium hydroxide precipitates (super-ficially charged) from positive to negative, for pH values over 8. These negative charges produce repulsion forces between the oil droplets (negatively charged) and the particles of precipitate, and consequently avoid the attachment of more than one droplet to a particle of precipitate, and the subsequent coalescence of the droplets, causing therefore decreases in the COD removal.

Fig. 5 shows the influence of the aluminium concentration on the COD removal and the steady state pH, in the chemical and the electrochemical continuous-coagulation experiments. It can be observed that the aluminium concentration necessary to attain the coalescence of the phases is slightly lower in the conventional process. However, the maximum values of COD removal obtained by both technologies are very similar. Regarding to the steady state pHs, it was observed that the pH values are slightly higher in the electrochemical process, despite the fact that the experiments were planned to achieve similar steady state pHs. This behaviour can be explained taking into account that in the conventional dosing process, the pH decreases with

the aluminium addition (initial pH 11.5), whereas in the electrochemical, this parameter increases slightly (initial pH 8.5). Many processes are related to these pH changes. Thus, in some cases it is almost impossible to obtain a more accurate behaviour of both processes.

The differences in the steady state pHs can explain the different efficiencies obtained by both technologies, in terms of the coagulant species. Thus, at pHs close to neutrality (steady state pHs in the conventional process) the particles of aluminium hydroxide precipitate should be positively charged. As well, this superficial charge changes to negative with increases in the pH (for pH values around 9). Therefore, at the steady state pH conditions of the conventional process, the charge of the precipitates can promote the linking of the oil droplets to particles of precipitate, favouring the coalescence of the oil droplets. However, the pH conditions in the electrocoagulation process are close to those in which the charge reversal takes place. This charge reversal would lead to negatively charged particles of precipitate, which would repeal the oil droplets, causing decreases in the efficiency. Despite this fact, no big differences are observed between the efficiencies attained by both (chemical and electrochemical) dosing technologies. As well, the values of zeta potential reached in these experiments were ranged between −15 and 10 mV, without fitting a general tendency. The behaviour observed in the COD removal denotes that the amount of aluminium necessary to produce the destabilization of the emulsion is proportional to the oil concentration.
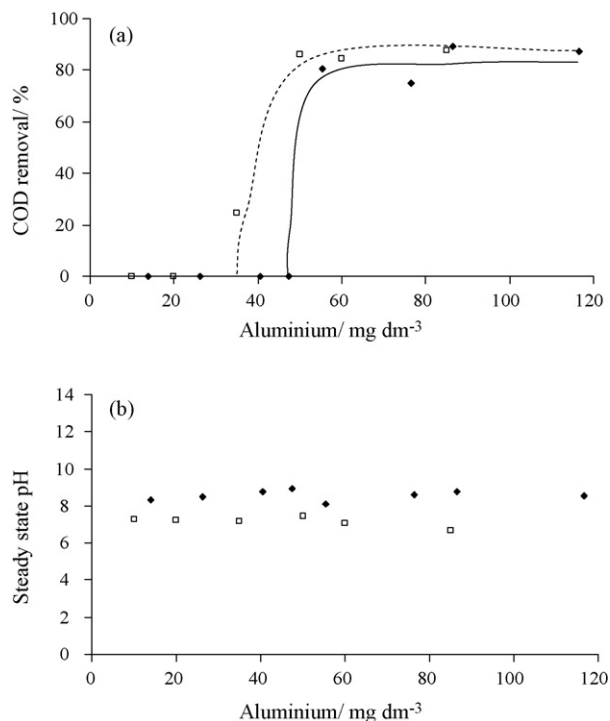

Fig. 5. Comparison between the chemical and the electrochemical continuous coagulation experiments as a function of the aluminium concentration added by both technologies. Temperature: 25 °C; oil concentration: $3000\ mg\ dm^{-3}$; supporting media: $3000\ mg\ NaCl\ dm^{-3}$. (♦) Electrochemical experiments, initial pH 8.5. (□) Chemical experiments, initial pH 11.5. (a) COD removal and (b) steady state pH.
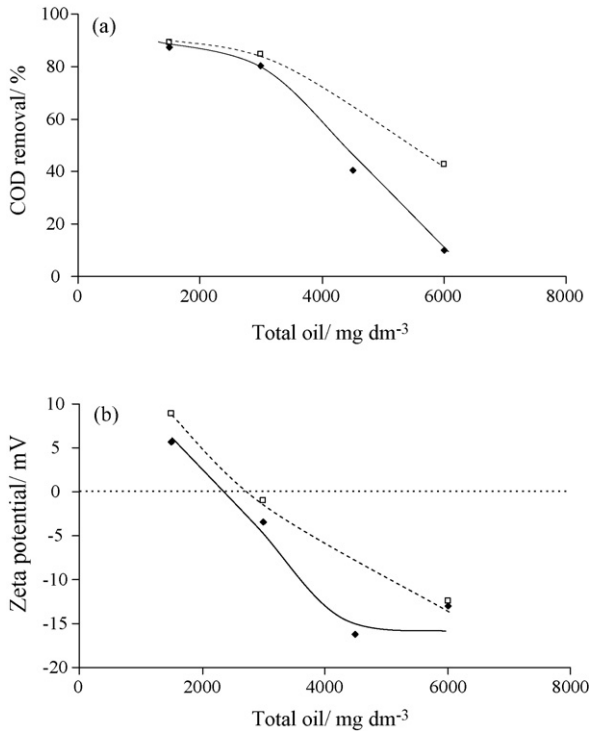
Fig. 6. Comparison between the chemical and the electrochemical continuous coagulation experiments in the treatment of O/W emulsions. Influence of the concentration of oil emulsified. Temperature: 25 °C; supporting media: 3000 mg NaCl dm^{-3}. (♦) Electrochemical experiments, current density: 10.1 mA cm^{-2}; initial pH 8.5. (□) Chemical experiments, initial pH 11.5. (a) COD removal and (b) Zeta potential.

Fig. 6 shows the comparison between the chemical and the electrochemical continuous coagulation experiments, as a function of the oil content, for similar conditions of aluminium concentration and pH in the steady state. It can be observed the same behaviour in chemical and electrochemical experiments: high oil concentrations lead to lower COD removals, being this effect more marked in case of the electrochemical process (lower efficiencies are obtained for high oil concentrations). Likewise, it can be observed that the zeta potential values reached in the steady-state are similar in both cases: they decrease with the oil concentration to negative values. The fact that the efficiency of the processes decreases with the oil content is consistent with the results obtained in the influence of the aluminium concentration, and it is indicative of a stoichiometric ratio between the oil removal and the aluminium added.

Fig. 7 shows the influence of the electrolyte in the continuous coagulation processes as a function of the aluminium concentration. As it can be observed, better results are obtained in the treatment of O/W emulsions containing chlorides than sulphates, for both, the chemical and the electrochemical technologies. Thus, the lowest efficiencies were attained by the electrochemical process in the treatment of emulsions in sulphate medium, whereas the highest COD removals were achieved by the chemical coagulation process in the treatment of chloride containing emulsions. To confirm the influence of the electrolyte in the coagulation process, some discontinuous chemical experiments (jar test) were carried out in both supporting media. Fig. 8 shows the COD
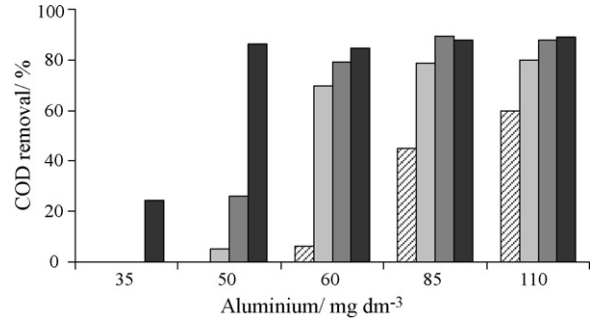

Fig. 7. Influence of the electrolyte in the chemical and the electrochemical continuous coagulation experiments in the treatment of O/W emulsions. Temperature: 25 °C; oil concentration: 3000 mg dm^{-3}. Supporting media 3000 mg Na$_2$SO$_4$ dm^{-3}, (▨) electrochemical experiments: initial pH 8.5; (▨) chemical experiments: initial pH 11.5. Supporting media 3000 mg NaCl dm^{-3}, (▨) electrochemical experiments: initial pH 8.5; (■) chemical experiments: initial pH 11.5.

removals as well as the zeta potential values, obtained in these batch experiments. As it can be seen, lower aluminium concentrations are required to attain the destabilization of the emulsion in chloride medium, whereas similar results are obtained in both media at high aluminium concentrations. Moreover, in chloride medium the zeta potential exceeds 0 mV for the experiments in which good removal percentages are reached, whereas in sulphate medium the zeta potential increases from −50 mV (the initial value) to attain less negative values (near 0 mV), but no positive values are attained (even by the experiments in which high efficiencies are reached). This fact is indicative of significant differences between both supporting media.
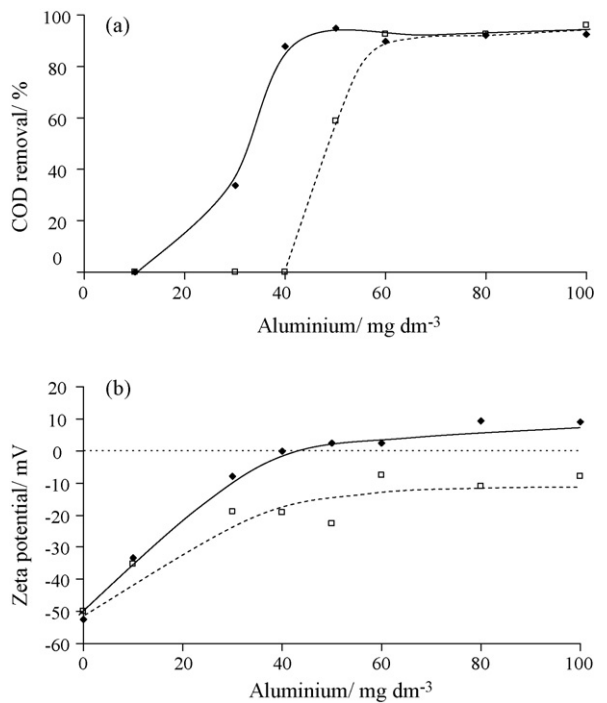

Fig. 8. Influence of the electrolyte in several chemical discontinuous coagulation experiments (jar test). Temperature: 25 °C; oil concentration: 3000 mg dm^{-3}; initial pH 11.5, (♦) supporting media: 3000 mg NaCl dm^{-3}, (□) 3000 mg Na$_2$SO$_4$ dm^{-3}.

The differences observed between both supporting electrolytes can be explained taking into account 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). This effect is more important in the presence of sulphate ions due to its higher charge, as it was observed in the aluminium speciation described in Supplementary data, which shows that the aluminium species formed in sulphate medium achieve negative zeta potentials in the range of pH studied, whereas in chloride media, only negative zeta potentials are obtained for pHs higher that 9. Consequently, this can explain the different results obtained in both media. The higher zeta potential values obtained (Fig. 8b) in the jar test experiments carried out in chloride media (for the same pH and aluminium conditions) are in agreement with this explanation. In this context, the smaller size of the chloride anion can help to explain by steric effects why a smaller amount of chloride ions are needed.

3.3. Influence of the operation mode in the chemical and electrochemical coagulation processes

To study the influence of the operation mode (continuous or batch) in the coagulation processes, several discontinuous experiments were carried out by recirculating the outlet of the reactor to the feed tank. Fig. 9 shows the discontinuous
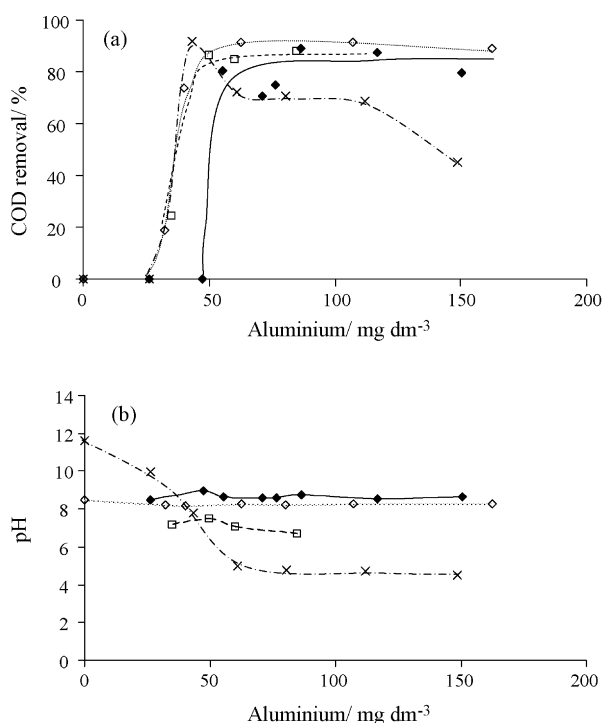
Fig. 9. Influence of the operation mode in the chemical and electrochemical coagulation processes. Temperature: 25 °C; oil concentration: 3000 mg dm^{-3}; supporting media: 3000 mg NaCl dm^{-3}. Electrocoagulation experiments, initial pH 8.5, (◆) continuous process, (◇) discontinuous process. Conventional coagulation experiments, initial pH 11.5, (□) continuous process, (×) discontinuous process.

chemical and electrochemical experiments compared to the continuous ones. The highest aluminium concentration necessary to achieve the break-up of the emulsion is observed in the continuous electrocoagulation process, although the maximum removal percentages obtained by all processes are similar. On the other hand, increases in the aluminium concentration cause important decreases in the efficiency of the chemical discontinuous process. This behaviour can be explained in terms of the changes in the pH observed in the experiments (shown in Fig. 9b). Thus, in the discontinuous conventional coagulation (in which the addition of aluminium is progressive), the pH decreases continuously during the experiment to values below 6, due to the acidic properties of the AlCl$_3$ added. These values of pH are out of the range of pHs in which the coagulation processes are efficient and this can explain the decrease in the COD removal. On the contrary, these changes of pH do not occur in the continuous coagulation processes, and neither in the discontinuous electrocoagulation process, as it can be seen in Fig. 8b. This explains the higher COD removals obtained in these latter processes.

Thus, according to the results obtained in this work, for a given case of the treatment of an O/W emulsion, it can be affirmed that the appropriate use of one of the processes (chemical or electrochemical) will be a function of the initial pH of the emulsion, and the pH required at the outlet of the treatment. So, in cases in that it is convenient a slight increase of the pH (together with the break-up of the emulsion and the coalescence of the phases), the electrocoagulation process will be the suitable alternative. On the contrary, if the initial pH of the emulsion (to be treated) requires a decrease from the initial value, the conventional coagulation process will be recommended. In any case, a bench-scale study would help to clarify the better technology to be applied for a given case.

4. Conclusions

From this work, the following conclusions can be drawn:

- The electrocoagulation and the conventional coagulation with hydrolyzing aluminium salts can be successfully applied to the treatment of oil-in-water emulsions. The efficiency of the processes does not depend directly on the dosing technology but on the total concentration of aluminium and pH. This latter parameter changes in a different way in the chemical and the electrochemical processes: the pH increases during the electrochemical experiments, but it decreases in the conventional one. It has been found that the break-up of the emulsion only takes place in the range of pHs between 5 and 9, and that the amount of aluminium necessary to produce the destabilization of the emulsion is proportional to the oil concentration. In addition, better efficiencies are obtained in the treatment of emulsions containing chloride ions as electrolyte, than those obtained in sulphate medium.
- The destabilization mechanism that allows explaining the experimental observations is the attachment of more than one oil droplet at a time to a positively charged particle of aluminium hydroxide precipitate, achieving that the organics

content in the linked droplets can be placed close enough to promote the coalescence of the oily phase.

- For the same aluminium concentration, the small differences observed between the chemical and the electrochemical processes can be explained in terms of the different changes in the pH that occurs in both processes. Therefore, a careful adjustment of the initial pH of the emulsion (that must be different for the chemical and the electrochemical processes) can achieve high COD removals by both coagulation technologies. These changes on the pH can also be influenced by the operation mode.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2007.05.043.

References

[1] M. Cheryan, N. Rajagopalan, Membrane processing of oily streams. Wastewater treatment and waste reduction, J. Membr. Sci. 151 (1998) 13–28.

[2] B.R. Kim, E.M. Kails, D.L. Florkey, S.L. Swatsenbarg, L. Luciw, C.H. Bailey, W.A. Gaines, J.H. Phillips, G.G. Kosokowsky, Evaluation of commercial ultrafiltration systems for treating automotive oily wastewater, Water Environ. Res. 70 (1998) 1280–1289.

[3] G. Rios, C. Pazos, J. Coca, Destabilization of cutting oil emulsions using inorganic salts as coagulants, Colloid Surf. A 138 (1998) 383–389.

[4] A.I. Zouboulis, A. Avranas, Treatment of oil-in-water emulsions by coagulation and dissolved-air flotation, Colloid Surf. A 172 (2000) 153–161.

[5] A. Pinotti, N. Zaritzky, Effect of aluminium sulphate and cationic polyelectrolytes on the destabilization of emulsified waste, Waste Manage. 21 (2001) 535–542.

[6] S.H. Shin, D.S. Kim, Studies on the Interfacial characterization of O/W emulsion for the optimization of its treatment, Environ. Sci. Technol. 35 (2001) 3040–3047.

[7] U.B. Ogutveren, S. Koparal, Electrocoagulation for oil–water emulsion treatment, J. Environ. Sci. Health A 32 (1997) 2507–2520.

[8] A.A. Al-Shamrani, A. James, H. Xiao, Destabilisation of oil–water emulsions and separation by dissolved air flotation, Water Res. 36 (2002) 1503–1512.

[9] L. Sánchez Calvo, J.P. Leclerc, G. Tanguy, M.C. Cames, G. Paternote, G. Valentin, A. Rostan, F. Lapicque, An electrocoagulation unit for the purification of soluble oil wastes of high COD, Environ. Prog. 22 (2003) 57–65.

[10] H. Inan, A. Dimoglo, H. Simsek, M. Karpuzcu, Olive oil mill wastewater treatment by means of electro-coagulation, Sep. Purif. Technol. 36 (2004) 23–31.

[11] M. Carmona, M. Khemis, J.P. Leclerc, F. Lapicque, A simple model to predict the removal of oil suspensions from water using the electrocoagulation technique, Chem. Eng. Sci. 61 (2006) 1233–1242.

[12] B.R. Kim, J.F. Zembla, S.G. Anderson, D.P. Stroup, D.N. Rai, Aerobic treatment of metal-cutting fluids wastewater, Water Environ. Res. 64 (1992) 216–222.

[13] P. Cañizares, J. García-Gómez, F. Martínez, M.A. Rodrigo, Evaluation of a simple batch distillation process for treating wastes from metalworking industries, J. Chem. Technol. Biotechnol. 79 (2004) 533–539.

[14] E. Dickinson, Interfacial interactions and the stability of oil-in-water emulsions, Pure Appl. Chem. 64 (1992) 1721–1724.

[15] I.F. Saur, S. Rubach, J.S. Forde, G. Kjaerheim, U. Syversen, Electroflocculation: removal of oil, heavy metals and organic compounds from oil-in-water emulsions, Filtr. Sep. 33 (1996) 295–303.

[16] A.Y. Hosny, Separating oil from oil-water emulsions by electroflotation technique, Sep. Technol. 6 (1996) 9–17.

[17] X.M. Chen, G.H. Chen, P.L. Yue, Novel electrode system for electroflotation of wastewater, Environ. Sci. Technol. 36 (2002) 778–783.

[18] P. Cañizares, F. Martínez, J. Lobato, M.A. Rodrigo, Electrochemically assisted coagulation of wastes polluted with eriochrome black T, Ind. Eng. Chem. Res. 45 (2006) 3474–3480.

[19] APHA-AWWA-WPCF, in: L.S. Clesceri, et al. (Eds.), Standard Methods for the Examination of Water and Wastewater, 17th ed., American Public Health Association, Washington, DC, 1989.

[20] D.R. Parker, P.M. Bertsch, Identification and quantification of the "Al_{13}" tridecameric polycation using ferron, Environ. Sci. Technol. 26 (1992) 908–914.

[21] S.J. Duffy, G.W. vanLoon, Characterization of amorphous aluminium hydroxide by the Ferron method, Environ. Sci. Technol. 28 (1994) 1950–1956.

[22] I.M. Solomentseva, S. Barany, J. Gregory, Surface properties and aggregation of basic aluminium sulphate hydrolysis products 1. Electrokinetic potential and hydration of BAS hydrolysis product particles, Colloid Surf. A 230 (2004) 117–129.

[23] P. Cañizares, F. Martínez, C. Jiménez, J. Lobato, M.A. Rodrigo, Comparison of the aluminium speciation in chemical and electrochemical dosing processes, Ind. Eng. Chem. Res. 45 (2006) 8749–8756.

[24] P. Cañizares, F. Martínez, J. Lobato, M.A. Rodrigo, Break-up of Oil-in-Water Emulsions by electrochemical techniques, J. Hazard. Mater. 145 (2007) 233–240.