The pH as a key parameter in the choice between coagulation and electrocoagulation for the treatment of wastewaters

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ABSTRACT

In this work, it is studied the influence of the pH of the waste in the coagulation with aluminum by conventional and electrochemical dosing. To do that, the speciation of aluminum as a function of the pH has been characterized, and this information has been used to interpret the results obtained in the treatments (by both coagulation methods) of a synthetic oil-in-water emulsion and an actual effluent of a door-manufacturing factory. Results show that a simple change in the pH of the wastes can result in a significant change in the efficiency of the coagulation process, and that if the same pH conditions are found at the end of the treatment, the efficiencies of the solution-dosing and of the electrochemical dosing technologies are very similar.

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1. Introduction

Coagulation/flocculation processes can be used to treat several types of waters and wastewaters, being among the most commonly treated the supply waters [1–3], the urban wastewaters, and wastewaters coming from different types of industries, such as those produced in the textile [4], chemical [5], pharmaceutical [6], metalworking [7] and petrochemical [8] factories.

Commonly, the conventional coagulation/flocculation processes involve three stages. In the first stage, chemical reagents are added to the wastewater, and these reagents produce the destabilization of the pollutants (or the formation of particles with reduced solubility from the pollutants). The aim of the second step is achieving the formation of solids with bigger size, and it is attained by a soft mix that allows the collision between particles and their aggregation. The last stage consists of the separation of the solids by settling or dissolved air flotation.

An alternative to the conventional process is electrocoagulation, which consists of the in situ generation of coagulants by the electrodissolution of a sacrificial anode, usually of aluminum or iron [9]. In this process, a proper design of the electrochemical cell allows carrying out the tree stages previously mentioned in a single compartment [10]. Thus, the electrodissolution of the sacrificial anode to the wastewater leads to the formation of hydrolysis products (hydroxo-metal species) that are effective in the destabilization of pollutants [11,12] and/or in the formation of particles with reduced solubility that entrap the pollutants [13]. As well, the electrochemical reduction of water in the cathode produces the formation of hydrogen bubbles that promote a soft turbulence in the system and bond with the pollutants decreasing their relative specific weight. Consequently, they enhance the flocculation process (electroflocculation) and the separation of the flocculated pollutants by flotation (electroflotation) [10]. In addition, the hydrogen can be collected and used as fuel in a fuel cell to produce energy. Other advantages reported in literature for the electrochemical process is the lower operating costs compared to the conventional process, due to the low electric current required [14,15].

In both coagulation processes (conventional and electrochemical) it is common the use of aluminum or iron reagents as coagulants [1–7,9–15]. When these reagents are added to the wastewater, different hydrolysis species are formed. According to literature [16–18], the main parameters influencing the speciation are the pH and the metal concentration. In this context, it is widely reported the formation of monomeric hydroxometallic ions that coexist with the metallic hydroxide precipitates. The aluminum hydroxide precipitate presents a minimum solubility in the region of pH 6 and the chemistry of monomeric ions is complex and it influences significantly on the coagulation process. On the contrary, ferric hydroxide precipitate shows a much lower solubility over a rather broad pH range and this limits the influence of the monomeric species on the coagulation results [16]. As well, in addition to these species, it is reported the formation of polymeric hydroxometal-

lic ions, especially under high metal concentrations [19,20]. All these hydrolysis metal species can interact with different types of pollutants, achieving their removal from the wastewaters. These interaction processes are strongly related to the metal speciation, and they can be summarized into three main types:

- The metallic ionic monomeric species can neutralize the charge of the pollutants by adsorption on their surfaces (or by binding to their ionized groups).
- The metallic ionic polymeric species can bind to several particles (or molecules) of pollutant at a time.
- The pollutants can be enmeshed into growing metallic hydroxide precipitates, or can be adsorbed onto their surfaces.

In this context, the goal of this work has been to study the influence of the pH in the coagulation with aluminum by conventional and electrochemical dosing. To do that, the speciation of aluminum as function of the pH has been characterized, and the knowledge have been used to interpret the results obtained in the treatment (by both coagulation methods) of a synthetic of oil-in-water emulsion and an actual effluent of a door-manufacturing factory. These results are used to study if a simple change in the pH of the wastes can result in a change in the efficiency, as well as if the same pH conditions at the end of the treatment would lead to similar efficiencies of the solution-dosing and of the electrochemical dosing technologies.

2. Experimental

2.1. Experimental devices

The electrocoagulation experiments have been carried out in a bench-scale plant with a single compartment electrochemical flow cell (Fig. 1). Aluminum electrodes were used as the anode and cathode. Both electrodes were square in shape (100 mm side) with a geometric area of 100 cm^2 each 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 wastewater was stored in a 5000 ml glass tank stirred by an overhead stainless steel rod stirrer HEIDOLPH RZR 2041 and thermostatized by means of a water bath, which allowed maintaining the temperature at the desired set point. The wastewater was circulated through the electrolytic cell by means of a peristaltic pump. The chemical experiments have been carried out in a bench-scale plant similar to the electrochemical one, where the electrochemical cell has been replaced by a single flow reactor (with the same geometry and without electrodes) and by including an aluminum solution (AlCl$_3$) dosage system with a peristaltic pump.

2.2. 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. Samples were taken at the outlet of the cell. In every case, after a time of settling (30 min), different measurements were made: COD (using a HACH DR2000 analyzer), zeta potential (using a Zetasizer Nano ZS, Malvern, UK) and pH (using an inoLab WTW pH meter). The aluminum concentration was determined by dilution (50:50, v/v) of samples with HNO$_3$ 4N and measured using an inductively coupled plasma Liberty Sequential Varian according to a standard method [21] (plasma emission spectroscopy).
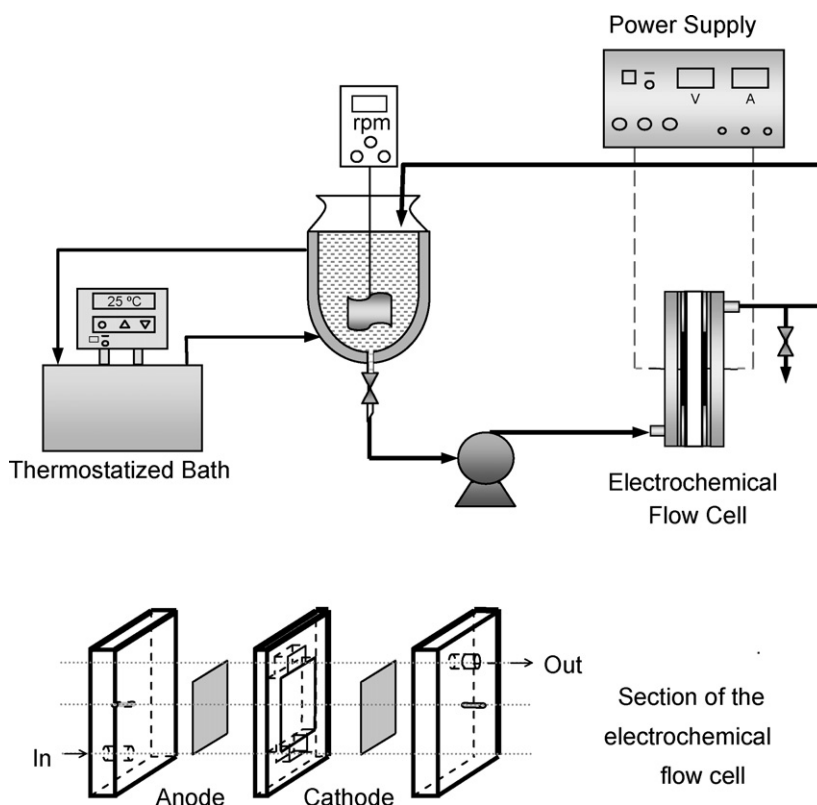

Fig. 1. Layout of the electrochemical coagulation bench-scale plant. Detail of the electrochemical flow cell.

2.3. Aluminum speciation

The characterization of the hydrolyzed aluminum species generated has been carried out by ferron method [22]. This method consists of the timed spectroscopy monitoring of aluminum ferron (8-hydroxy-7-iodo-5-quinolinesulfonic acid) reaction, to form a complex of probable composition [17] Al(ferron)$_3$ 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 has been carried out by filtering the samples using micropore membranes of 0.45 μm in order to remove the particles of precipitate. Once the sample is filtered, an aliquot is added to volume of saturated ferron solution freshly prepared (as ferron is not stable [22]) 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 aluminum vs. time, the ratio of aluminum species that react quickly and slowly with ferron (that is, monomeric and polymeric species) can be estimated. Extrapolation of the linear parts of the curve to zero time yields information on the amount of aluminum that is bound in complexes of different degree of polymerization [22]. The measurement of total and soluble aluminum (filtered with 0.45 μm) reports the ratio of soluble and precipitate aluminum.

2.4. Preparation of the synthetic oil-in-water emulsion

The oily phase of the synthetic 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) 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 3000 mg dm^{-3}.

2.5. Door-manufacturing process (DMP) wastewater

The actual effluent used in this work comes from the gluing process of a door-manufacturing factory in which the main reagent is formaldehyde/urea. This effluent contains a high concentration of COD (typical range around 10,000–15,000 mg dm^{-3}), total nitrogen (typical range 300–400 mg N dm^{-3}) and suspended solids (typical range 12,000–15,000 mg dm^{-3}). The main characteristics of the sample used in this work are summarized in Table 1.

To study the influence of the pH in the improvement of the coagulation results, the pH of the wastewaters (O/W emulsion and

Table 1
Main characteristics of the raw effluent of the wooden-door manufacturing factory (DMF) studied in this work
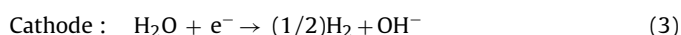
Parameter	Value
COD$_0$ (mg dm^{-3})	13,068
pH	7.2
Conductivity (mS cm^{-1})	7.5
Total Nitrogen (mg N dm^{-3})	347
Suspended solids (mg dm^{-3})	13,574
Main pollutants	Formaldehyde/urea

DMP waste) was modified prior to feed them to the coagulation processes, by adding NaOH or HCl for the pH adjustment.

3. Results and discussion

3.1. Changes in the solution pH with the aluminum dosing

To study the influence of the pH in the conventional and electrochemical dosing of coagulants, several experiments were carried out by adding aluminum with both dosing methods. In a first stage, the effect of the aluminum dosing method on the pH of an aqueous solution of sodium chloride was studied. This solution did not contain any pollutants in order to avoid any interference from the coagulation processes (adsorption of aluminum species, protons or hydroxyl anions, ion exchange processes, etc.). Fig. 2 shows the changes recorded in the pH with the aluminum dosing. It can be observed a very different change of the pH with both technologies: the pH increases during the electrochemical dosing, whereas it decreases during the conventional one. The different changes in the pH during the dosing can be explained in terms of the dosing products. It is not feasible to dose aluminum hydroxide by solution pumping due to the low solubility of this species. Hence, typically sulphate or chloride salts are used to dose the aluminum. The acidic properties of these salts (caused in fact by the hydrolysis of the Al^{3+} cation) explain the decreases in the pH of the solution. Conversely, the electrochemical dosing technology produces Al(OH)$_3$ as net product (Al^{3+} on the anodic surface and OH$^-$ on the cathodic surface, Eqs. (1)–(3)) and this generates a completely different system from the viewpoint of the hydrolysis of aluminum species that can explain the increases of the pH.

$$\text{Anode}: \quad Al \rightarrow Al^{3+} + 3e^- \tag{1}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{2}$$

$$\text{Cathode}: \quad H_2O + e^- \rightarrow (1/2)H_2 + OH^- \tag{3}$$

The final pH difference between both dosing technologies is over 3 points and obviously this will have to influence on the speciation of aluminum in the reaction system. This observation is confirmed in Fig. 3, where it is shown the effect of the pH on the zeta potential of the solids formed during the dosing processes. As there are not pollutants in the reaction system, aluminum hydroxide species are the only solids present in the system, and the positive and negative values of the zeta potential are caused by the adsorption of cationic or anionic hydroxoaluminum species, respectively. Both, the data corresponding to the salt solution and the electrochemical dosing lies
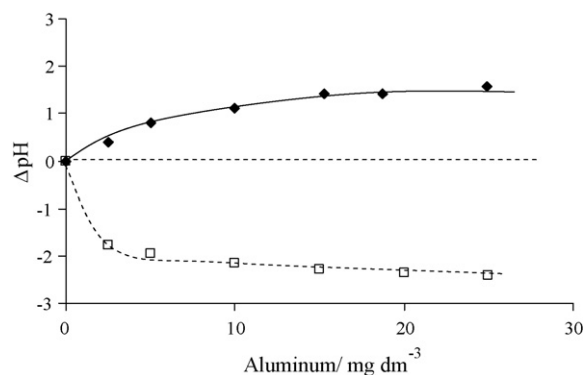

Fig. 2. Influence of the dosing technology on the changes in the pH. Changes in the pH with the addition of aluminum to aqueous (NaCl) solutions by conventional and electrochemical dosing. Temperature: 25 °C; supporting media: 3000 mg NaCl dm^{-3}; initial pH of the solution ~7. (♦) Electrochemical dosing and (□) conventional dosing.
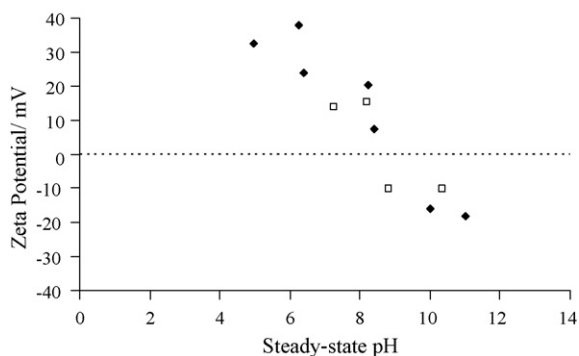
Fig. 3. Influence of the pH on the zeta potential achieved in an electrochemical and in a conventional coagulation process. Temperature: 25 °C; supporting media: 3000 mg NaCl dm^{-3}. (♦) Electrochemical dosing and (□) conventional dosing.

Fig. 4. Influence of the pH on the aluminum species formed in chemical and electrochemical continuous experiments. Temperature: 25 °C; supporting medium: 3000 mg NaCl dm^{-3}; flow rate: 19 dm^3 h^{-1}. Monomeric hydroxo-aluminum ions: (■) electrochemical dosing and (□) conventional dosing. Polymeric hydroxo-aluminum ions: ···▲··· electrochemical dosing and ···#··· conventional dosing. Aluminum hydroxide precipitates: - -♦- - electrochemical dosing and - -◊- - conventional dosing.

over the same trend, and it seems clear that the precipitate is positively charged for pHs under 8 and negatively charged for higher pHs. Hence, there is not a difference of the solid species formed for the same pH conditions (for both technologies), but there is a significant difference in the pH of the treated waste. This can have a strong influence on the coagulation results, especially in cases where there is not pH control. For example, for the trapping of a negatively charged pollutant a coagulation treatment which leads to a pH below 8 will be more efficient than a coagulation treatment in which the pH is higher, as there can be more possibilities of interaction because of the opposite charge of the coagulant reagent and of the pollutants.

The pH also influences on the monomeric species formed, as it is shown in Fig. 4. However, there are not significant differences in the speciation obtained by the solution dosing and the electrochemical dosing technologies for the same pHs. It is clear that the aluminum hydroxide precipitate only influences between pHs 5 and 9 and outside this range, only ionic species have to be considered to explain the coagulation results. In this context, the influence of polymeric species is very limited as compared to the monomeric species as they are only significant for pHs around 5, and even for such pHs their concentration is three times smaller than that of the monomeric ionic species.

3.2. Coagulation of O/W emulsions and DMP wastewaters

To test the effect of a modification in the pH on the results of a coagulation process, in this work two different types of wastewaters have been used. One consists of a synthetic O/W emulsion and the other in an actual wastewater polluted with a high concentration of colloids and suspended solids. Previous experiments were carried out for both wastes in order to determine the optimum doses
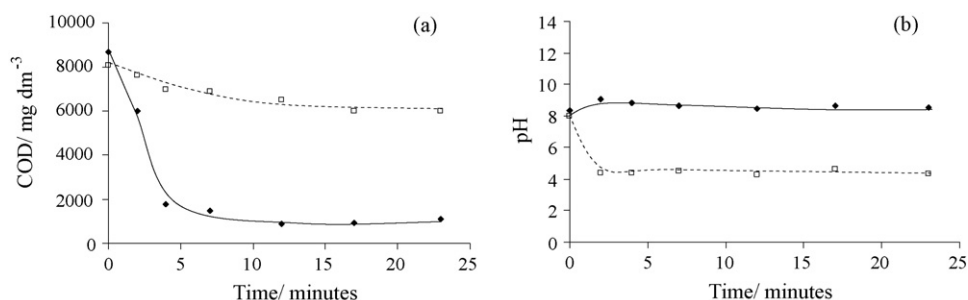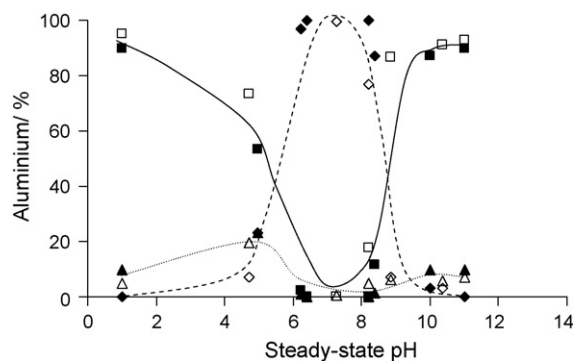
of aluminum (150 and 60.0 mg dm^{-3} for DMP and O/W wastes, respectively). These doses were afterwards used for both dosing technologies, by the choice of the right current intensity (electrocoagulation) and of the right reagent pumping rate (conventional coagulation).

Fig. 5 shows the time-course of the COD and pH during the coagulation of the O/W emulsion with the two dosing technologies. It can be observed that both, the changes in the pollutant concentration and in the pH, are very different. Electrochemical dosing of aluminum achieves good removal efficiencies in the steady-state (removal efficiency over 70%). On the contrary, in case of the conventional dosing, low decreases in the COD are obtained with the addition of the same dose of aluminum. Changes observed in the pH are as expected. In the electrochemical dosing experiment the pH increases slightly up to finally reach a value around 8.5, whereas in the conventional dosing of aluminum the pH decreases markedly down to 4.4. Fig. 6 shows the results obtained in the treatment of the DMP wastewaters. A similar behavior is obtained for both coagulation technologies, although in this case the removal efficiencies are slightly smaller for the electrochemical treatment. The changes in the pH are less significant than those observed in the treatment of the O/W emulsion. This can be explained in terms of a more significant presence of weak acids and/or bases that buffer the pH (like the carbonate/bicarbonate couple) in the waste, which according to Fig. 3 leads to a smaller change of pH. Nevertheless, the pH decreases in the chemical process down to a value below 7, while in the electrochemical one it increases up to pH 7.8.

A first point that should be marked from these results is that none of the processes is better than the other for all wastes. Elec-

Fig. 5. Time courses of the continuous coagulation and electrocoagulation of the raw synthetic O/W emulsions. Temperature: 25 °C; oil concentration: 3000 mg dm^{-3}; flow rate: 10.7 dm^3 h^{-1}; aluminum concentration (steady-state): 60 mg dm^{-3}; supporting media: 3000 mg NaCl dm^{-3}. (♦) Electrochemical experiment, current density: 10.1 mA cm^{-2}. (□) Conventional dosing experiment.
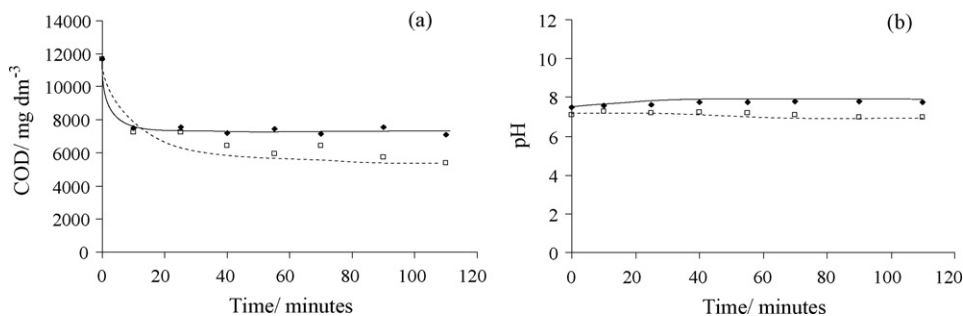
Fig. 6. Time courses of the continuous coagulation and electrocoagulation of the raw DMP waste. Temperature: 25 °C; flowrate: 50 dm³ h⁻¹; volume: 1.5 dm⁻³. (♦) Electrochemical experiment: current density: 1 mA cm⁻². (□) Conventional dosing experiment.

trochemical coagulation obtained better results in the case of the O/W emulsion but the results reverse in the case of the DMP. Other important point is the significant change of the pH during the treatment, even in the case of wastes with a high conductivity (DMP wastes) in which some species can buffer the pH. A third point that should be noted is that although the doses of reagents and the fluid dynamic conditions are the same for both dosing technologies the changes in the concentration of pollutants are different. This has to be a consequence of the different pH of the treated wastes.

3.3. Improvement of the coagulation results with a modification in the pH

In the previous section, it was observed that efficiencies obtained by coagulation and by electrocoagulation differ significantly. To check if a change in the pH can improve the results, the technology that obtains the worse results in the treatment of the O/W emulsion (coagulation) and of the DMP waste (electrocoagulation) was fed with the corresponding pH-modified waste (the

same waste in which the pH was modified in order to achieve the same pH at the steady-state). Figs. 7 and 8 show the results obtained in both cases. It can be observed that to reach approximately the same steady-state pH (that electrocoagulation) the pH of the O/W emulsion fed to the coagulation process has to be increased up to 11.5 (+3.2 units). Likewise, to attain approximately the same steady-state pH that coagulation, the pH of the DMP wastes has to be decreased down to 6.5 (−1.1 units) before the electrocoagulation treatment. In both cases, the steady-state pHs do not match exactly, as the matrix effects make almost impossible to attain these conditions. However, they are close enough to explain the good reproducibility in the COD removal. From these results, it can be pointed the very strong influence of the pH on the coagulation processes. It can also be remarked that both coagulation processes can obtain the same removal efficiencies when they work under similar steady-state pH conditions.

The improvement of the results obtained by the coagulation technology in the case of the O/W emulsion can be easily explained in terms of the contribution of the positively charged hydroxide pre-
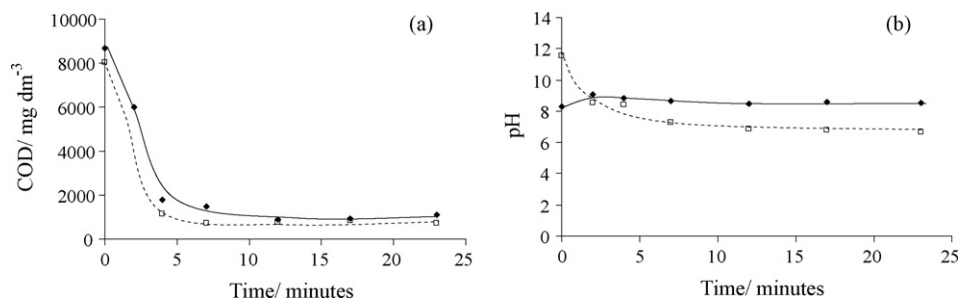

Fig. 7. Time courses of the continuous coagulation and electrocoagulation of the pH-modified O/W emulsions. Temperature: 25 °C; oil concentration: 3000 mg dm⁻³; flow rate: 10.7 dm³ h⁻¹; aluminum concentration (steady-state): 60 mg dm⁻³; supporting media: 3000 mg NaCl dm⁻³. (♦) Electrochemical experiment: current density: 10.1 mA cm⁻². (□) Conventional dosing experiment, initial pH of the emulsion: 11.6.
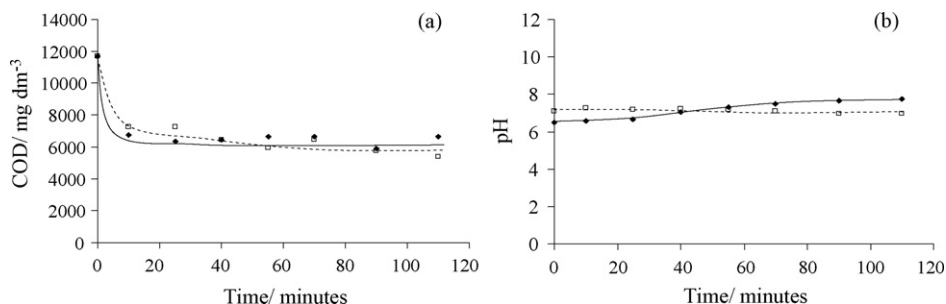

Fig. 8. Time courses of the continuous coagulation and electrocoagulation of the pH-modified DMP. Time courses of the coagulation and electrocoagulation of the pH-modified synthetic oil-in-water emulsions with aluminum. Temperature: 25 °C; volume: 1.5 dm⁻³. (♦) Electrochemical experiment: initial pH of the water: 6.5; current density: 1 mA cm⁻². (□) Conventional dosing experiment.

cipitate in the breakup of the emulsion (main species formed during the electrocoagulation process according to Figs. 3 and 4). Thus, 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 aluminum hydroxide precipitate, achieving that the organics content in the linked droplets can be placed close enough to promote the coalescence of the oily phase. If the pH of the emulsion is not changed, the main coagulant species dosed during the non-electrochemical coagulation process are monomeric and polymeric cations (according to Fig. 4) which are not effective in the breakup of the emulsion. However, the change in the pH of the waste previous to its treatment allows achieving the same reagents than those obtained with the electrocoagulation process and so, the same efficiencies.

In the case of the DMP waste, the higher efficiency obtained by the coagulation (when the pH of the waste is not modified) has also to be explained in terms of the contribution of the aluminum hydroxide precipitates. These are the more significant coagulant species for pHs around 6.5. From there, the concentration of monomeric anionic species increases rapidly with the pH, reducing the proportion of amorphous aluminum precipitates. Thus, the smaller efficiency observed in the case of the electrochemical process can be caused by the higher steady-state pH obtained in the process, that makes that the proportion of precipitate (that is the main coagulant species) diminish. Consequently, a decrease in the pH of the DMP before the electrocoagulation allows increasing the ratio of precipitate species and with this, the efficiency of the process.

Therefore, due to the different changes in the pH, in case of the treatment of a given wastewater by conventional or electrochemical coagulation, the initial pH of the wastewater will be decisive for the efficiency obtained in each coagulation process. This is explained because the concentration of reagent and the pH determine the particular coagulant species, and depending on the characteristic of the pollutants these species can be effective in the removal of pollutants or not. In this way, the unitary cost of the aluminum dosed by both technologies is very similar and a simple modification in the pH, like the ones shown in this paper can make a given technology more attractive than the other from a simple economic viewpoint. Thus, the price of aluminum sheets (Al 1050) is around $3.85 \, \text{€} \, \text{kg}^{-1}$ Al. The cost of dissolution depends on the intensity and cell potential but for a typical case ($1.5 \, \text{mA} \, \text{cm}^{-2}$, $1.5 \, \text{V}$) and taking into account an efficiency of 150% (over the expected Faraday value, according to literature [23]) this results in $4.15 \, \text{€} \, \text{kg}^{-1}$ Al. As it can be noted, this cost is in the same range that the cost of aluminum sulphate (100% $Al_2(SO_4)_3 \cdot 14H_2O$) and aluminum polychloride (solution of 40% in Al_2O_3) which are 4.51 and $2.83 \, \text{€} \, \text{kg}^{-1}$ Al, respectively.

In addition, the pH required at the outlet of the coagulation treatment can also be important. If the treated waste is going to be discharged to the environment or a sewer, the pH is limited by regulations. If the treated waste is going to be fed to other process, sometimes a modification of the pH should be desired in order to use it in the best conditions. In both cases, the modification of the pH has associated costs, and they can be reduced by selecting the right coagulation technology. Thus, in the cases in that it is convenient a slight increase of the pH (together with the removal of the pollutants), the electrocoagulation process will be the suitable alternative. On the contrary, if the initial pH of the wastewater 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, and it has to be taken in mind that this modification of the pH should be a secondary goal and not the primary one (the removal of the pollutants).

4. Conclusions

From this work the following conclusions can be drawn:

(a) The pH has a significant influence on the coagulant species formed during coagulation processes. It also has influence on the superficial charge of the aluminum hydroxide precipitates (caused by the adsorption of ionic species).
(b) During the time-course of coagulation and electrocoagulation processes, the pH changes in an opposite way and this affects significantly to the coagulant species formed, and hence to the efficiencies obtained in the removal of pollutants.
(c) It cannot be said that any process is better than the other for all wastes. Under the same fluid dynamic conditions, doses of aluminum, and pHs, the efficiencies obtained by coagulation and electrocoagulation are very similar.
(d) The pH of the waste can be a key parameter in the choice of the coagulation technology. The unitary cost of aluminum by both technologies is very similar and a strong modification of the pH (like the one required by the coagulation technologies to increase their efficiency) can advice against the use of this technology.

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