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On the crucial influence of some supporting electrolytes during electrocoagulation in the presence of aluminum electrodes

J.L. Trompette*, H. Vergnes

Laboratoire de Génie Chimique UMR 5503, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France

ABSTRACT

The influence of some supporting electrolytes on aluminum electrode oxidation and pH variation during electrocoagulation of an unskimmed milk sample and a cutting oil emulsion has been investigated. Among the electrolytes studied, sulfate anions were found to be quite harmful both for electrical consumption and electrocoagulation efficiency. At the opposite, chloride and ammonium ions were particularly benefic respectively for aluminum corrosion and pH regulation, whereas sodium cations were observed to have a neutral role.

The results indicate that electrocoagulation can be realized at low anodic potential even in the presence of sulfate ions when the $[Cl^-]/[SO_4^{2-}]$ ratio is around or greater than 1/10. The detrimental effect of sulfates on electrocoagulation efficiency can be thwarted by the use of the ammonium salt thanks to its related buffer effect.

1. Introduction

In the literature numerous studies have been devoted to the treatment of fluids of different nature through the electrocoagulation process with aluminum plates as sacrificial electrodes [1–3]. Owing to its recognized properties: convenience, cheapness, safety, ecological, this electrochemical technique has gained a renewed attention due to the growing quest for both economical and environmental interests [4]. However this technology remains complex since its performances are modulated by the interplay of electrochemical, physicochemical and hydrodynamic parameters. At the molecular level, one of the key point to achieve an efficient separation is to control the behavior and the influence of the diverse ionic species that are present in the medium.

During electrocoagulation with aluminum electrodes, the following basic electrolytic reactions take place:

the release of Al^{3+} ions, accompanied with the oxidation of water, at the anode:

$$Al \rightarrow Al^{3+} + 3e^- \qquad (1)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (2)$$

the reduction of water on the cathode through:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (3)$$

Depending on the Al^{3+} ion concentration, the solution pH and also ageing, consecutive hydrolysis reactions can generate the formation of monomeric hydroxides such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, $Al(OH)_4^-$ and some polymers as $Al_6(OH)_{15}^{3+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{34}^{5+}$ [1,5]. As it has been well recognized [5,6], the pH plays a major role in electrocoagulation process. Indeed the nature and thus the efficiency of the coagulating species are intimately related to the pH level in the system. As a result of many investigations on the subject [5,7,8], it has been argued that the most probable species that are responsible for electrocoagulation efficiency in the pH range 5–9.5 are polymeric hydroxoaluminum ions and the $Al(OH)_3$ aluminum hydroxide precipitate. These two coagulating agents may have a coercive action. Polymeric cations can adsorb onto the negatively charged colloidal particles (droplets) so promoting aggregation through charge neutralization and/or bridging flocculation. The resulting aggregates can be enmeshed in the extended and open amorphous hydroxide precipitate ('sweep flocculation' process) [5]. In the same time, the small electrogenerated hydrogen bubbles coming from water reduction at the cathode favor the flotation of aggregates, so allowing an easier removal.

Whereas the previous species, that are electrogenerated in situ, have to promote the coagulation of dispersed colloids (particles or droplets), some electrolytes that are most often added to adjust the

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* Corresponding author. Tel.: +33 5 62 88 58 59; fax: +33 5 61 55 61 39.
E-mail address: jeanluc.trompette@ensiacet.fr (J.L. Trompette).

electrical conductivity of the fluid to be treated, may also interact with the electrodes where the essential electrolytic reactions are expected to take place. Indeed when aluminum electrodes are used, some characteristics have to be taken into account. In contact with atmosphere aluminum develops on its surface an insulating film of alumina (Al_2O_3) due to natural oxidation with oxygen gas. This surface oxide film, which is stable in the pH range 4–10 in aqueous media, has been reported to be constituted of an adherent compact layer covered with a more porous layer [9]. Despite sulfate anions are passive agents for aluminum surfaces so preserving the surface oxide layer [10], which complicates the formation of coagulating aluminum cations, several studies use sulfate electrolytes to confer a sufficient electrical conductivity [11–17]. This causes a waste of electrical energy (high imposed potential values) to allow the breakage of the passive film in order to obtain satisfying treatment conditions. At the opposite, common electrolytes such as NaCl, are often used for conductivity reasons but without anticipating the powerful corrosive properties of chloride ions that promote, even at low concentrations, film breakdown through pitting corrosion [9].

In order to investigate the influence of the nature of ions, electrocoagulation experiments were performed at the laboratory scale on two kind of fluids: unskimmed milk and cutting oil, by using different supporting electrolytes: NaCl, Na_2SO_4, NH_4Cl, $(NH_4)_2SO_4$ at the same 0.01 M concentration. Milk is a natural sable emulsion that contains original chloride ions. In milk, the dispersed fat droplets are stabilized by the anionic and amphiphile casein proteins. Cutting oils are synthetic fluids that are used in mechanical operations of machining metals owing to their cooling and lubrication properties [18]. These emulsions are produced in concentrated forms and are later diluted with water. The basic formulation of cutting oils is composed of a mineral oil, emulsifiers, and various additives to resist against corrosion and bacterial growth. However the detailed composition of these very stable emulsions remains often a home-made secret. As the efficiency of cutting fluids decrease with repeated use, due to thermal degradation and the presence of metallic residues, they have to be changed periodically. Due to environmental requirements these effluents have to be treated to remove organic wastes and significant amount of surfactants. Among the various techniques that are used, electrocoagulation has been found to be quite interesting both for economical and environmental reasons [6,12,19,20].

In the present study, the comparative separation efficiency during electrocoagulation was appreciated through the measurement of pH values, the determination of the percentage of COD removal and the observation of sample aspects during run time.

2. Experimental

2.1. Materials

Ammonium chloride (NH_4Cl), sodium chloride (NaCl), ammonium sulfate ($(NH_4)_2SO_4$) and sodium sulfate (Na_2SO_4) were obtained from Sigma–Aldrich (France) and were used as received. Deionized water was taken as a solvent.

Unskimmed bovine milk (Candia, France) was used as a representative natural stable emulsion. The original pH and conductivity were respectively 6.7 and 4 mS/cm. A sample of 4 g of unskimmed milk was diluted to obtain 100 mL of liquid to be studied with a 0.01 M electrolyte concentration. The measured zeta potential for dilute milk samples was around – 25 mV at pH 6.9.

Emulstar FX15 (Gillot-Larcher, France) was used as a representative cutting oil emulsion ($\rho = 0.88$ g/mL). As recommended for practical use, it was diluted at 5% v/v in aqueous solution and then homogenized under magnetic agitation at 800 rpm during 15 min. The measured zeta potential for dilute Emulstar samples was around – 80 mV at pH 8.3.

2.2. Methods

The electrochemical set up was constituted with two parallel aluminum plates as anode and cathode and a mercury sulfate reference electrode (MSE). Both aluminum electrodes were cut from a commercial sheet (A-U4G, Al alloy 2017 containing 4% w/w of Cu) to obtain small plates with a rectangular shape (2 cm × 3 cm × 0.2 cm). A new pair of aluminum electrode was used for each experiment; the surfaces were thoroughly polished with emery paper and then immersed in acetone. After rinsing with water, they were immersed (2.5 cm depth) in 100 mL of liquid in a glass vase and were 1 cm spaced. The immersed area of each electrode used was 11.4 cm^2 (2 × (2.5 cm × 2 cm) for the faces + 2 × (2.5 cm × 0.2 cm) for the lateral sides + 2 cm × 0.2 cm for the bottom side). Moderate agitation was imposed with a magnetic stirrer at 400 rpm during electrocoagulation or electrolysis experiments [21]. This compromise value was chosen since it promotes the encounter between the colloids and the destabilizing species without causing any perceptible break-up of the resulting aggregates within the used experimental device.

The electrical current was applied using a potentioscan (Radiometer Analytical S.A. Copenhagen, Tacussel DEA 332, potential range 0–9 V) coupled with a digital converter (Radiometer Analytical, IMT 102) and controlled by a PC running the electrochemical software (Radiometer Analytical, VoltaMaster 2). The imposed current intensity was checked to be constant during each electrocoagulation experiment with the use of an amperemeter (Metrix MX 55C). All the experiments were repeated twice.

The pH and the conductivity were measured respectively with an electronic pH-meter (Hanna Instrument) and a Tacussel electrode (Tacussel Instrument).

The COD levels were determined using the standardized colorimetric technique (Hach, Germany) with an excess of chromium trioxide in sulfuric acid in glass vials and subsequent measurement of the optical density. The initial COD concentrations of the dilute unskimmed milk sample and the cutting oil emulsion are respectively 8000 and 115,000 mg/L.

A 3 CCD digital video camera, Panasonic NV-GS 120 (Crystal Engine), was used to film the behavior during electrocoagulation experiments.

3. Results and discussion

3.1. Competitive behavior of chlorides and sulfates

The chloride concentration in unskimmed milk was found to be 0.027 M (say about 0.95 g of Cl^-/L of milk, which is in the range of expected values [22]). For that purpose, the standard method for the determination of chloride, 4500 Cl^- B. Argentometric method was used.

Thereafter 100 mL of dilute aqueous milk solutions with increasing volume of unskimmed milk and containing the same 0.01 M concentration of ammonium sulfate salt were prepared. The $[Cl^-]/[SO_4{}^{2-}]$ ratio and the conductivity of the different milk solutions are reported in Table 1. For each sample, the current intensity was recorded as a function of time when a working electrode potential of 8 V/MSE was applied. The results are presented in Fig. 1 (the numbers next to the curves refer to the % in volume of milk in Table 1).

The high difference in the observed levels of current intensity cannot be related to the small variation in solutions conductivity

Table 1
Percentage in volume of unskimmed milk in solution and corresponding value of the $[Cl^-]/[SO_4^{2-}]$ ratio and sample conductivity

	% v/v of milk				
	0	1	2	3	4
$[Cl^-]/[SO_4^{2-}]$ ratio	0	0.027	0.054	0.081	0.108
Conductivity (mS/cm)	2.1	2.22	2.31	2.33	2.36

(see Table 1); moreover the curves exhibit different shapes. In the absence of milk (see curve 0 in Fig. 1), the intensity decreases fast and stabilizes to a very low value, around 2 mA, and very poor gas evolution was observed at electrode surfaces. This reflects the pronounced effect of the passive film which is not attacked by sulfate ions, so preventing the significant release of Al^{3+} ions. When 1 mL of milk is used (see curve 1 in Fig. 1), the intensity decreases also and reaches a value of about 20 mA, so indicating that the amount of chloride ions is not sufficient to oppose the passive action of sulfates. For 2 and 3 mL of milk (see respectively curves 2 and 3 in Fig. 1), there is a minimum: the current intensity begins to decrease but after many seconds it increases (with more difficulty for curve 2) and it was observed to level off for much longer times. This suggests that some sulfate anions begin to be first adsorbed onto the aluminum anode, probably in regard of their double ionic charge (they are more attracted), but when chlorides can satisfactorily approach the surface, their oxidative effect, through pitting corrosion, becomes irreversible. For 4 mL of milk (see curve 4 in Fig. 1), corresponding to the ratio $[Cl^-]/[SO_4^{2-}]$ >0.1 (see Table 1), the corrosive power of chloride is predominant: the current intensity increases rapidly and remains definitively constant at the expected level depending on the solution conductivity.

Although in a recent study [23] it was indicated that a minimum Cl^- concentration of 60 ppm, say 1.7×10^{-3} M, was required to breakdown the anodic passive film of an aluminum electrode placed in sulfate salt solutions at a notified 1 g/L concentration (say 7×10^{-3} M), the results obtained in the present work suggest that the pertinent criterion is rather the $[Cl^-]/[SO_4^{2-}]$ ratio. This parameter reflects the competitive character of both ions; the well-shaped curves that are recorded in cases where this ratio is lower than 0.1 advocate in this sense.

In order to strengthen this statement, complementary electrolysis experiments were conducted in the same conditions by varying this ratio at well define values for synthetic aqueous solutions containing sodium chloride and sodium sulfate, see Table 2. The results are shown in Fig. 2 (the numbers next to the curves refer to the type of solution in Table 2). Whatever the amount of Cl^- ions, equal or lower than the claimed value of 1.7×10^{-3} M [23], the predominant oxidative effect of chloride during electrolysis, characterized by the steep increase of current intensity and the following constant level, is found to occur only when the $[Cl^-]/[SO_4^{2-}]$ ratio is around or greater than 1/10. As expected, the constant current intensity is proportional to the corresponding solution conductivity. The characteristic shape of the curves, relative to different $[Cl^-]/[SO_4^{2-}]$ ratios, was controlled to remain the same when the exposed surface area of aluminum electrode in contact with solution was varied.

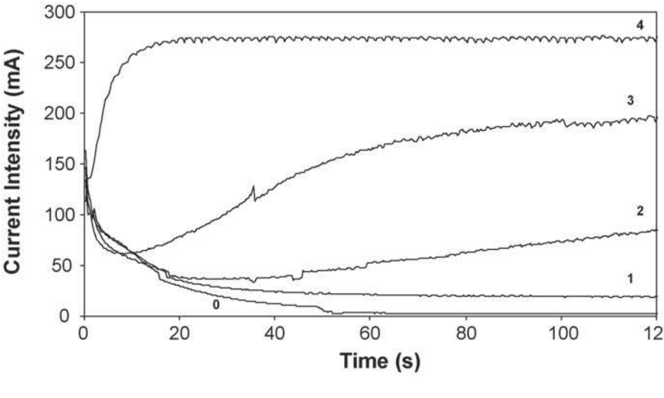

Fig. 1. Variation of the current intensity as a function of time for the different milk solutions when a working electrode potential of 8 V/MSE is applied.

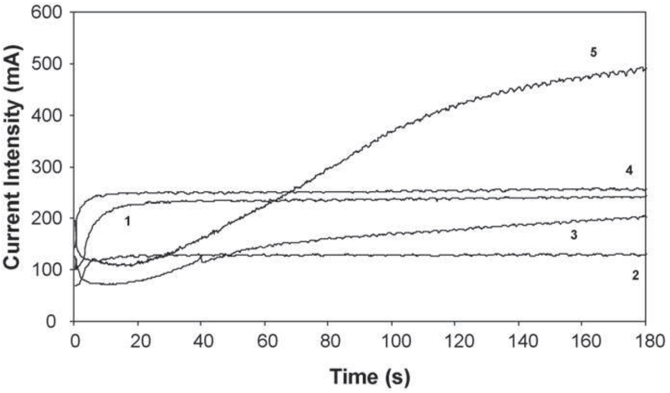

Fig. 2. Variation of the current intensity as a function of time for the different synthetic electrolyte solutions when a working electrode potential of 8 V/MSE is applied.

From these results it is confirmed that if sulfate salts are used as supporting electrolytes, electrocoagulation can be operational at low potential (under 10 V/MSE) only when a sufficient amount of corrosive species is originally present or is added in the fluid to be treated. In the case of corrosive chloride ions, the $[Cl^-]/[SO_4^{2-}]$ ratio should have to be around or greater than 0.1. When sulfate salts are the sole electrolytes, very high voltage need to be applied to allow the breakage of the passive film, and this corresponds to a significant waste of electrical energy [23]. For instance, it was recorded with the punctual use of a DC power supply (potential range 0–400 V) that a working electrode potential of 40 V/MSE (corresponding to a cell voltage of about 60 V) was required to impose a 0.2 A current intensity in the presence of Na_2SO_4 at 10^{-2} M, whereas it was reduced to about 7 V/MSE when using a solution with Na_2SO_4 at 10^{-2} M + NaCl at 10^{-3} M.

At this level it has to be emphasized that ion-dependent corrosive properties have been rarely taken into account in electrocoagulation studies although they may be responsible of important consequences in electrical power consumption and electrocoagulation efficiency. Up to date the influence of electrolyte nature has consisted in comparing the obtained results when testing different electrolytes at various concentrations to assess the optimum dosage [6,24].

3.2. *Comparative electrocoagulation of milk samples*

In light of the precedent results, the comparative electrocoagulation behavior of milk solutions, with a 4% v/v of unskimmed milk and a 0.01 M sulfate salt concentration, was investigated at a 0.2 A imposed current intensity. Within this condition the concentration of chloride ions is around 10^{-3} M.

In the case of ammonium sulfate, flocculation begins at 12′ and the mixing of greater flocs is clearly observable at 14′30″ where the electrode surfaces can be distinguished (Fig. 3a). When experiment is stopped at 16′, the flocs are rapidly collected at the top and a clear bottom phase is observed at 16′30″ (Fig. 3b). The situation is radically different with sodium sulfate. Although some aggregates have been formed, no significant flocculation is observed in the bulk.

Table 2
Type of synthetic electrolyte solution: NaCl and Na_2SO_4 concentration, and corresponding value of the $[Cl^-]/[SO_4^{2-}]$ ratio and solution conductivity

	Solution				
	1	2	3	4	5
NaCl in mol/L	1×10^{-3}	5×10^{-4}	5×10^{-4}	1.7×10^{-3}	1.7×10^{-3}
Na_2SO_4 in mol/L	1×10^{-2}	5×10^{-3}	1×10^{-2}	1×10^{-2}	3.4×10^{-2}
$[Cl^-]/[SO_4^{2-}]$ ratio	0.1	0.1	0.05	0.17	0.05
Conductivity (mS/cm)	2.02	1.15	1.96	2.1	6.09

Only a weak clarification can be detected from 20′ (Fig. 4a); the solution remains turbid up to the end, say 35′ (Fig. 4b). As expected the COD levels confirm these trends, see Fig. 5a. The COD removal stabilizes at 84% from 16′ with ammonium whereas it reaches tediously 60% after 30′ with sodium salt.

The origin of such differences becomes clear through the measurement of pH values at regular time intervals, see Fig. 5b. Starting from 6.9 in the presence of both electrolytes, the pH rises respectively to 8.3 and 9 for ammonium and sodium after 4′. Whereas it stabilizes at 8.7 from 8′ with ammonium, the pH values are observed to increase continuously with sodium and to exceed 10 for longer times.

As it was evidenced in a recent study [21], the interpretation of these results is ascribed to the impact of the buffer effect of the ammonium/ammonia couple on pH regulation. The hydroxyl ions (OH^-) that are generated at the cathode, through water reduction, are not only consumed with the released Al^{3+} but also through an irreversible reaction with the ammonium cations according to:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \quad (4)$$

As a consequence of the production of ammonia (NH_3), the corresponding acid–base equilibrium (pK = 9.2) associated to its buffer effect takes place through:

$$NH_3 + H^+ \leftrightarrow NH_4^+ \quad (5)$$

In these conditions, the pH is maintained at a level where the formation of $Al(OH)_4^-$ complexes, which are largely inefficient for the flocculation of negatively charged colloidal entities, is precluded and the proportion of efficient coagulating aluminum species is greater [5].

From these results it is found that separation is effective in less than 20′ when using ammonium sulfate whereas it is very difficult with the corresponding sodium salt. Indeed electrocoagulation was observed to remain inefficient even when a greater current intensity, say 0.4 A, was applied in the presence of sodium sulfate. Here also the pH values were found to increase continuously and to exceed 10.

To inspect more deeply the influence of electrolyte nature, the same comparative experiments were performed within the same

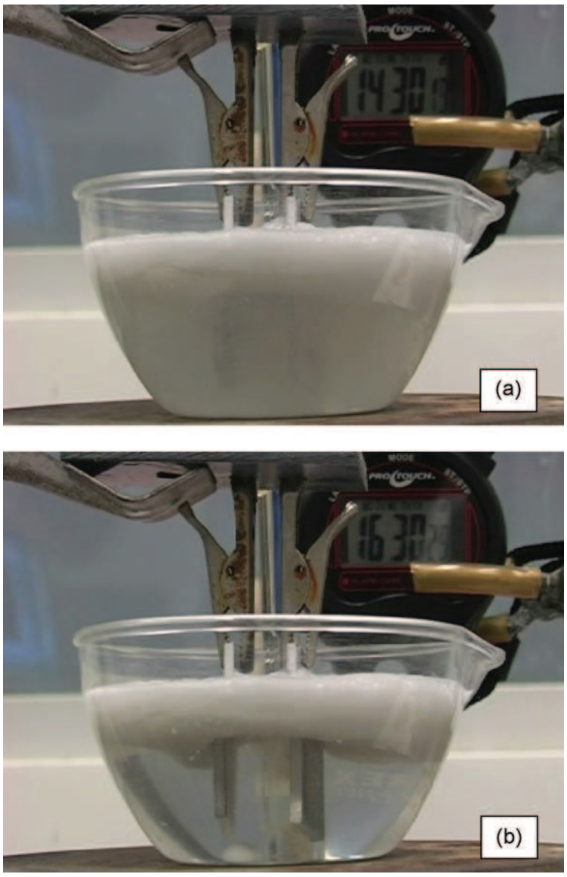

Fig. 3. Photographs during electrocoagulation of milk sample at 0.2 A in the presence of ammonium sulfate at 14′30″ (a), 16′30″ at rest (b).

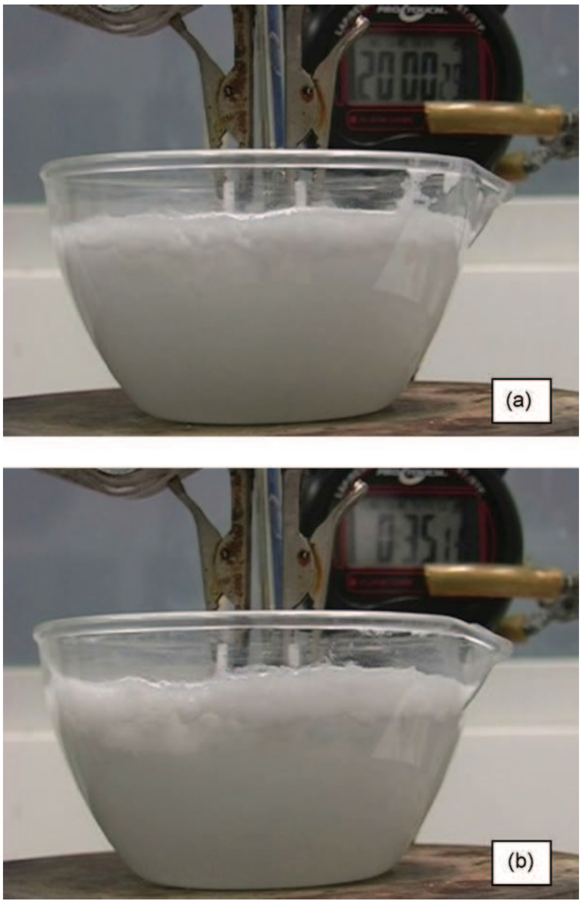

Fig. 4. Photographs during electrocoagulation of milk sample at 0.2 A in the presence of sodium sulfate at 20′ (a), 35′ (b).

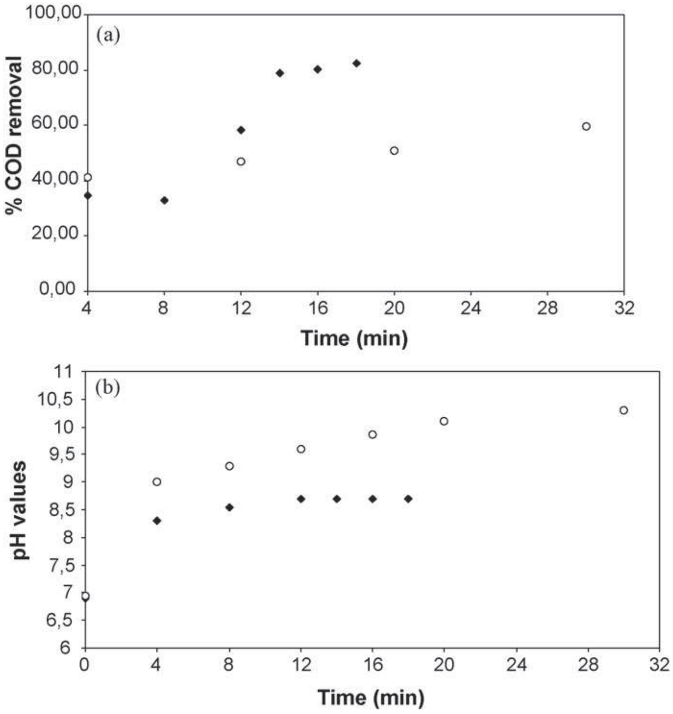

Fig. 5. Compared variation of the % COD removal (a) and pH values (b) as a function of time for ammonium sulfate (◆) and sodium sulfate (○) during electrocoagulation of milk sample at 0.2 A.

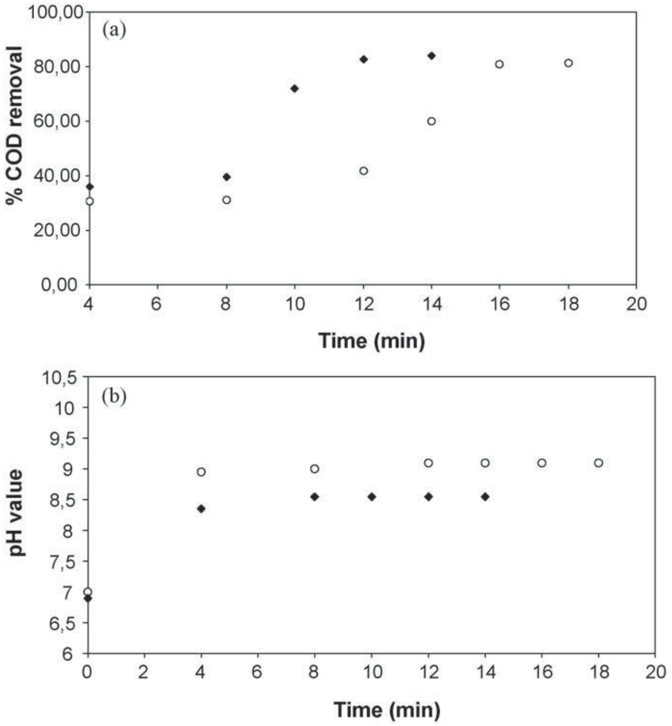

Fig. 6. Compared variation of the % COD removal (a) and pH values (b) as a function of time for ammonium chloride (◆) and sodium chloride (○) during electrocoagulation of milk sample at 0.2 A.

conditions in the presence of ammonium and sodium chlorides. The electrocoagulation is effective in this case with sodium salt. The final level of COD removal is approximately the same as that was reached with ammonium chloride but it is obtained about 4 min later, see Fig. 6a, for the same pH reasons as invoked above. This means that the electrical consumption is between 25 and 30% greater with sodium chloride. As few differences are observed between the pH values for both ammonium electrolytes, see Figs. 5b and 6b, the separation efficiency is effectively of the same order at the end. Nevertheless it can be noted that it is obtained earlier in the case of ammonium chloride, say 12′ instead of about 15′ with ammonium sulfate, see Figs. 5a and 6a. However the difference becomes very large when sodium salts are compared. The pH for sodium chloride seems to stabilize at around 9; it does not increase continuously as in the case with sodium sulfate, see Figs. 5b and 6b.

The comparative variation of pH values during electrolysis of sodium electrolyte solutions was investigated. To be within the same concentration range as in the case of milk samples, electrolysis was performed with a synthetic solution composed of Na_2SO_4 at 10^{-2} M + NaCl at 10^{-3} M and a synthetic solution containing NaCl at 10^{-2} M + NaCl at 10^{-3} M. Whereas the pH is found to reach a nearly constant value of 8.7 with chloride solution, it increases continuously in the presence of sodium sulfate and approaches 10, see Fig. 7. These results corroborate those obtained with milk solution and indicate the non-influence of milk content. These measurements clearly show that the pH increase is more pronounced in the presence of sulfate ions and this may be, at least partially, one of the reasons why electrocoagulation is so poor.

It has been already pointed out [1,6] that better electrocoagulation efficiency was obtained in the presence of chloride electrolyte than with sulfates, however the origin of this behavior still remains an open debate [6,23]. Contrary to chloride, sulfate ions have been argued to promote the formation of hydroxide precipitates over the formation of polymeric cations, so reducing the extent of particle aggregation. Moreover it was assumed that the ions could adsorb onto the surface of aluminum precipitates and/or screen the surface charge of polymeric cations [6,8,25]. In both cases the presence of sulfates is expected to disfavor particles capture. It has been also proposed that the supporting ions could eventually exchange partly with OH^- in the $Al(OH)_3$ precipitate so provoking a pH increase [25]. According to this assumption the obtained results would indicate an enhanced exchange with sulfate anions than with chlorides.

Nevertheless and interestingly, the results indicate that even when sulfate ions are present, one way to overcompensate their harmful effect on separation efficiency is to use preferentially the ammonium salt. The situation is much more improved due to the supplementary consumption of OH^- ions.

3.3. Application to cutting oil emulsion

The studied Emulstar emulsion does not contain any chloride ion (as an indication, the conductivity increases from the beginning if

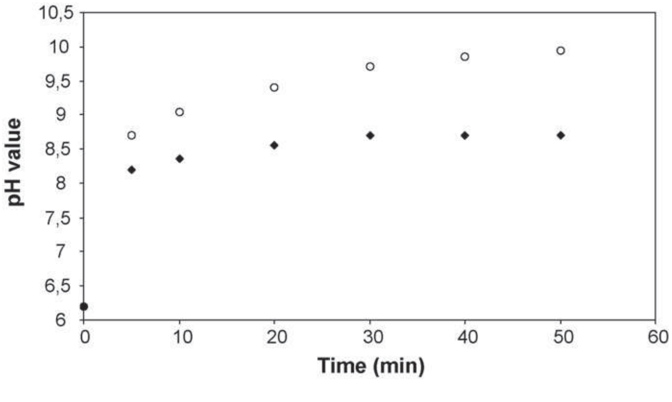

Fig. 7. Variation of the pH values as a function of time during electrolysis at 0.2 A of synthetic solution with Na_2SO_4 at 10^{-2} M + NaCl at 10^{-3} M (○) and solution with NaCl at 10^{-2} M + NaCl at 10^{-3} M (◆).

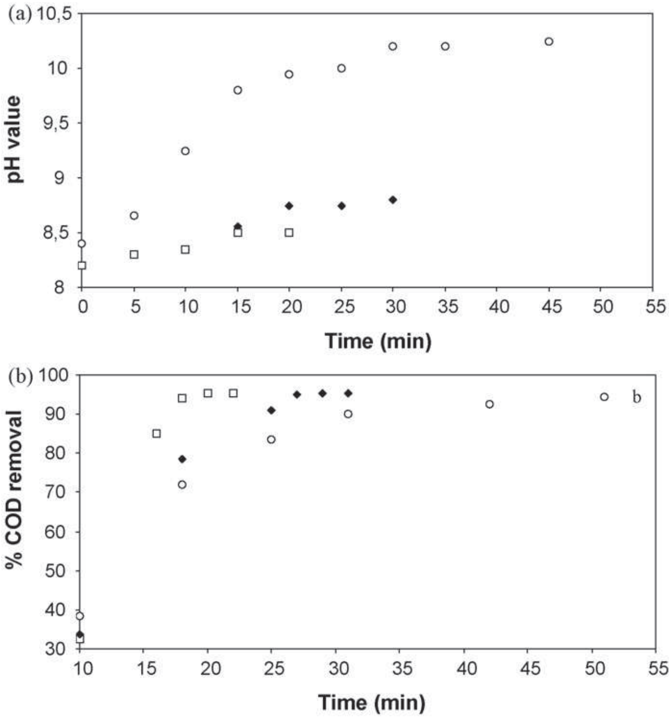

Fig. 8. Compared variation of the pH values (a) and % COD removal (b) as a function of time during electrocoagulation of Emulstar sample at 0.3 A in the presence of electrolyte A (♦): $(NH_4)_2SO_4$ at 10^{-2} M + NH_4Cl at 10^{-3} M; electrolyte B (○): Na_2SO_4 at 10^{-2} M + NaCl at 10^{-3} M; and electrolyte C (□): NH_4Cl at 10^{-2} M.

$AgNO_3$ is added). As such when sulfate salts are used as supporting electrolyte and if it is decided to operate with a low electrical energy consumption, say with an applied potential lower than 10 V/MSE, it becomes therefore necessary to add some chloride salt to obtain satisfactory separation efficiencies.

In order to emphasize the influence of electrolyte nature, the electrocoagulation behavior of Emulstar emulsion at 5% v/v has been studied at an imposed 0.3 A current intensity in the presence of different supporting electrolytes, referred as A: $(NH_4)_2SO_4$ at 10^{-2} M + NH_4Cl at 10^{-3} M; B: Na_2SO_4 at 10^{-2} M + NaCl at 10^{-3} M; and C: NH_4Cl at 10^{-2} M. The variation of the pH values and the % COD removal are reported respectively in Fig. 8a and b.

Through its buffer effect, the presence of ammonium in A and C helps to stabilize the pH values under 9 even when sulfates are present (see Fig. 8a), so that the proportion of expected coagulating agents is greater. However NH_4Cl is found to exhibit the best results. As it was already mentioned in Section 3.1, the presence of sulfates delays the obtaining of the same level of % COD removal at the end, see Fig. 8b. It is approximately 10 min earlier in the case of C with respect to A, which corresponds to a gain of electrical consumption of about 30%. This suggests that sulfate anions in solution hinders the efficiency of the coagulants probably through the enhanced screening of the positive charge of the polymeric hydroxoaluminum cations and/or through their adsorption onto the $Al(OH)_3$ amorphous precipitate, as it has been evoked in previous studies [6,25].

Even though the pH slightly exceeds 10 in the case of B, the separation efficiency becomes comparable in term of % COD removal to that obtained with A and C. Nevertheless the time required in the case of B is very long (see Fig. 8b) and thus prohibitive for usual treatments.

As an indication the qualitative aspect of each sample at the end of electrocoagulation treatment is shown in Fig. 9.

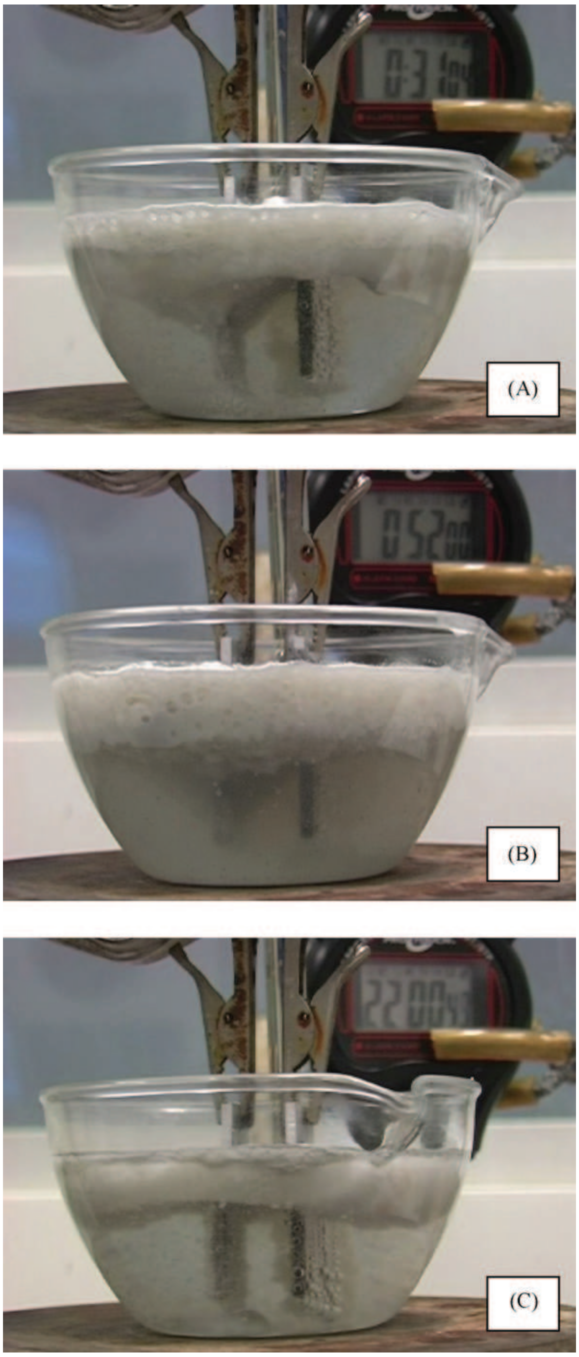

Fig. 9. Photographs of Emulstar sample at the end of electrocoagulation treatment at 0.3 A in the presence of electrolyte A: $(NH_4)_2SO_4$ at 10^{-2} M + NH_4Cl at 10^{-3} M; electrolyte B: Na_2SO_4 at 10^{-2} M + NaCl at 10^{-3} M; and electrolyte C: NH_4Cl at 10^{-2} M.

It has to be noted that although the % COD removal is quite good (about 95%), the final COD values are still high: about 5700 mg/L for A and C and 6900 mg/L for B. This indicates that although electrocoagulation has allowed to obtain clarified aqueous solutions through the break-up of cutting oil emulsions, supplementary treatments are required before eventual discharging into the environment.

4. Conclusions

In light of the obtained results, it has to be insisted that electrocoagulation in the presence of sulfates should be avoided when operating with aluminum electrodes since sulfates anions have a harmful influence on electrical consumption and electrocoagulation efficiency. Indeed, due to their passive action regarding aluminum oxidation, they imply that very high electrical potential need to be applied to breakdown the alumina passive film if they are the sole supporting electrolyte or if the proportion of corrosive species is too low. When corrosive chloride ions are originally present or have to be added, the ratio $[Cl^-]/[SO_4^{2-}]$ should be around or greater than 0.1 to ensure a sufficient release of aluminum cations, so allowing further satisfactory separation conditions even when operating at low electrical potential, say lower than 10 V/MSE.

During electrocoagulation, sulfates cause indirectly a pH increase which renders the separation efficiency more difficult. However this can be favorably thwarted by the use of the ammonium salt. The gain in electrical consumption is about 30%. Nevertheless sulfate ions in the bulk may also hinder the efficiency of the coagulating agents through charge screening of the cationic coagulating agents.

Owing to the impact of the buffer effect of ammonium on pH regulation and the significant corrosive power of chlorides, NH_4Cl is expected to be one of the most relevant supporting electrolytes to obtain better and faster electrocoagulation efficiency in the presence of aluminum electrodes.

Acknowledgments

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