

Organic matter removal from oil-water emulsions by electrocoagulation - 1. Thermodynamic analysis

Remoção de matéria orgânica de emulsões óleo-água por eletrocoagulação - 1. Análise termodinâmica

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Resumo

Uma análise termodinâmica da remoção de matéria orgânica (DQO) de emulsões sintéticas óleo-água, pelo processo de eletrocoagulação, foi feita com o objetivo de determinar as espécies iônicas mais estáveis, em diferentes condições de pH e concentração de alumínio, de modo a identificar os possíveis mecanismos de remoção. A análise sugere que as espécies predominantes, durante o estágio reativo, são o hidróxido de alumínio amorfo (para a especiação mononuclear do alumínio) e a espécie trimérica positivamente carregada, $Al_3(OH)_4^{5+}$ (para a especiação polinuclear do alumínio). A desestabilização da emulsão, provavelmente, ocorre por meio de neutralização de carga, conduzida, conjuntamente, pela espécie polinuclear e por partículas de hidróxido de alumínio positivamente carregadas. Esse mecanismo de sorção deve ser o mecanismo primário de coagulação, durante o estágio reativo. Pode haver também a formação de precipitados de hidróxido e/ou óxido de alumínio, durante o estágio de estabilização, o que sugere a modificação gradual do mecanismo dominante de remoção para floculação por varredura (*sweep flocculation*).

Palavras-chave: Eletrocoagulação, emulsões óleo-água, matéria orgânica (DQO), termodinâmica.

Abstract

A thermodynamic analysis of the organic matter (chemical oxygen demand - COD) removal from synthetic oil-water emulsions by the electrocoagulation process was performed with the objective of determining the most stable ionic species under diverse pH and aluminum concentration conditions and identifying possible removal mechanisms. The analysis suggests that the predominant species during the reactive stage are the amorphous aluminum hydroxide (for the mononuclear speciation of aluminum) and the positively charged trimeric species, $Al_3(OH)_4^{5+}$ (for the polynuclear speciation of aluminum). The emulsion destabilization probably occurs by charge neutralization, carried out jointly by the polynuclear species and by positively charged aluminum hydroxide. This sorption mechanism is likely to be the primary coagulation mechanism during the reactive stage. The formation of

aluminum hydroxide and/or oxide during the stabilization stage may also take place, which indicates the gradual change of the dominant removal mechanism to sweep flocculation.

Keywords: Electrocoagulation, oil-water emulsions, organic matter (COD), thermodynamics.

1. Introduction

Oil-water emulsions are widely used in metal industries in processes such as rolling, forging and shaping, because they exhibit properties that include lubrication, surface cooling, cleaning and corrosion prevention. According to Carmona et al. (2006), the main problem with such emulsions is their substantial degradation with time at work temperatures, which are normally between 45°C and 90°C. The emulsions must therefore be regularly replaced, often several times a year. They have oil contents in the range 0.1 - 30 kg.m⁻³, depending on the specific application, are toxic and must be treated so that recycling of water is possible.

Several electrochemical methods have been studied over the years for the separation of oil-water emulsions (Yang,

2007; Cañizares et al., 2008, Ibrahim et al., 2001, Kramer et al., 1979). Electroflotation was one of the first processes developed in which oil is removed from emulsions previously destabilized by chemical additives. More recent efforts have been focused on the application of electrochemical techniques to destabilize (“break”) the emulsion and separate the destabilized oil without the addition of chemical reagents. The key process involved in most of these techniques is electrocoagulation which can be considered a two-stage process: (1) aluminum or iron ions are electrolytically produced to reduce the repulsive forces on the negatively charged oil droplets and break the emulsion; (2) a direct-current tension is applied through the emulsion to set off the migration and coalescence

of the droplets. Cañizares et al. (2008) observed that the gas bubbles generated in electrocoagulation (oxygen at the anode and hydrogen at the cathode) promote the coalescence (electroflocculation) and the separation of coalesced droplets, which may be carried to the top of the emulsion and then collected and removed.

In this work, a thermodynamic analysis of the organic matter removal from synthetic oil-water emulsions by electrocoagulation was performed with the objective of determining the most stable ionic species at the different conditions of pH and aluminum concentration and identifying possible removal mechanisms. The organic matter was measured by the chemical oxygen demand (COD).

2. Materials and methods

Oil-water emulsions

The oily phase of the tested emulsion is regular lubricant oil (Shell Talpa 30). To prepare the emulsion, both sodium oleate and oil (0.5 - 10 kg.m⁻³) were mixed and

stirred at 1500 rpm for 8 hours until a homogeneous liquid was obtained. Next, the supporting electrolyte which consisted of NaCl solutions in distilled water was added to increase

the conductivity of the emulsion. The pH of the emulsion was around 8.7. The emulsion was stored in a 5 L glass tank stirred by an overhead stainless steel rod stirrer.

Experimental Apparatus

The experimental setup is shown in Figure 1. The system consisted of an electrochemical cell and a direct current power supply. The emulsion was magnetically stirred at 250 rpm to ensure homogenization. Two digital multimeters were used for measuring the current passing through the circuit and the applied potential. The pH was monitored with a pH-meter. All experiments were carried out at room temperature (25 ± 1°C) and

under galvanostatic conditions.

The electrocoagulation unit was made of acrylic with the following dimensions: 150 mm long, 190 mm wide and 170 mm high. The cell was equipped with four electrode plates, two aluminum anodes and two 316L stainless steel cathodes, which were fully submerged. The electrodes were 120 mm long, 130 mm wide and 1 mm thick and were perforated uniformly with a 5 mm drill

bit to facilitate the movement of emulsion inside the cell. Taking into account the volume occupied by the magnetic rod at the bottom of the reactor and the totally submerged electrodes, the actual volume of the cell was 5 L. Generally, the cell was operated in monopolar mode, which means that all the electrodes were physically connected to either the positive or the negative outlet of the dc power supply.

Experimental Procedure

The experiment started with the introduction of the emulsion into the cell. The initial pH was adjusted to the desired value (4-12) with aliquots of HCl or NaOH. A given current density within

the 1.11 mA.cm⁻² - 17.79 mA.cm⁻² range was then applied to the cell. Samples were collected at regular 5 minute intervals and the emulsified organic concentration was measured to determine the process

efficiency. The pH was also measured at the same time intervals. The initial and final weights of the aluminum plates were measured to determine the total amount of aluminum dissolution.

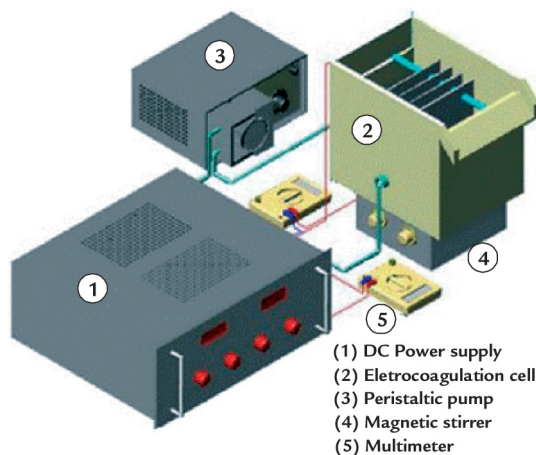


Figure 1
Schematic diagram of
the experimental setup.

3. Thermodynamic analysis

A thermodynamic analysis of the removal of organic matter (COD) from synthetic oil-water emulsions was conducted with the HSC software (Chemical Reaction and Equilibrium Software by HSC Chemistry) to determine the most stable ionic species at different pHs and aluminum concentrations. This allowed identifying possible mechanisms involved in electrocoagulation. Eh-pH diagrams were constructed to examine the stability of aluminum in solution and its dissolution behavior. The analysis initially considered an aluminum-water system with mononuclear species and precipitated aluminum hydroxide and later a system with hydroxy-complex species. The thermodynamically stable state (minimum Gibbs free energy) and consequently the final equilibrium composition was predicted.

The concentration gradients vary continuously during electrocoagulation since the aluminum continues to dissolve and release ions in solution. To properly assess the changes that occur over a batch electrocoagulation run, three ranges of

concentrations were taken into account. These ranges correspond to the inertia, reactive and stabilization stages that were observed in the curves of COD reduction and percent removal of organic matter as a function of time.

The first range corresponds to the stage of inertia when the aluminum concentration is less than the minimum required concentration to cause oil removal. This concentration range relates to the beginning of the electrocoagulation process. Aluminum concentrations inferior to 0.1 kg.m^{-3} were experimentally chosen. At low aluminum concentrations (inertia stage) the oil is not removed and if the initial pH of the emulsion is less than 11 there is only an increase of the coagulant concentration and pH. The concentration of coagulant due to the dissolution of aluminum and pH augments as the water is reduced to hydrogen and hydroxyl ion. Even at this early stage, aluminum hydroxide is thermodynamically stable as predicted by the Eh-pH diagram shown in Figure 2.

The second range is associated

with the reactive stage, i.e., when the concentration of aluminum is higher than the minimum concentration and lower than the concentration at which there no longer occurs oil removal from the emulsion (stabilization stage). Experimental data indicated that the concentrations of aluminum in this range are between 0.1 kg.m^{-3} and 0.2 kg.m^{-3} . At these intermediate concentrations the aluminum hydroxide becomes the dominant species, which should result in passivation of the aluminum anodes. However, the experimental results contradict this argument, which may be explained by the fact that chloride ions inhibit the formation of a passivation layer (Holt, 2003). Nevertheless, the inclusion of such ions in the thermodynamic analysis does not change the boundaries of predominance. It should be emphasized that the thermodynamic analysis does not consider the electrodes passivation kinetics. Consequently, it is expected that the electrodes undergo passivation over a long period of time.

The pH for the electrocoagulation experiments was stabilized between 9.0

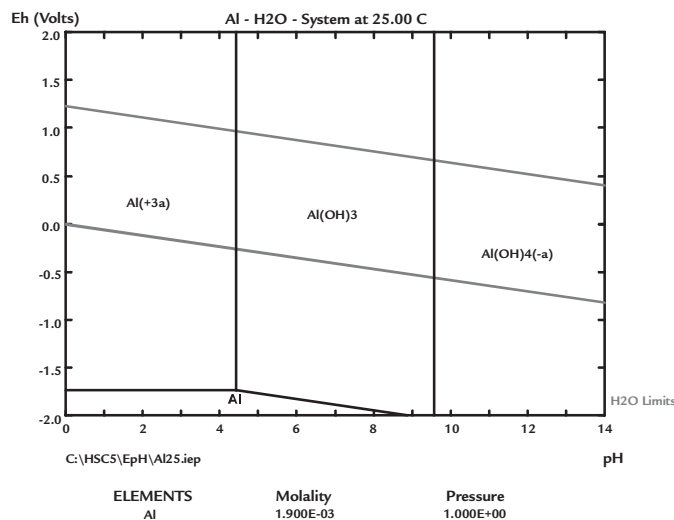


Figure 2
Eh-pH diagram for the inertia
stage of electrocoagulation.

and 10.0 depending on the initial pH of the emulsion. This pH range corresponds to the interface between the solid aluminum hydroxide and the aluminate ion ($\text{Al}(\text{OH})_4^-$), as indicated in Figure 3. The proximity of this interface to the operating pH implies that the $\text{Al}(\text{OH})_4^-$ anion may deteriorate the performance of the process.

The third range relates to the stabilization stage when further increases in the concentration of aluminum do not result in subsequent increases in oil removal. Experimental observation revealed that the concentrations of aluminum in such range are in excess of $0.2 \text{ kg}\cdot\text{m}^{-3}$. In high concentrations of aluminum the predominance region of the aluminum hydroxide has become wider, as shown in Figure 4. The operating region for the electrocoagulation corresponded to that of aluminum hydroxide precipitation. In the concerned range the area of aluminum hydroxide predominance increased with the total concentration of aluminum. Even if the aluminum oxide (Al_2O_3) was included in the thermodynamic analysis, as will be done next, its precipitation also coincides with the electrocoagulation

operating region. Thus, a precipitate of aluminum hydroxide or aluminum oxide was thermodynamically expected.

The beginning of the reactive stage can be defined as the point where there is a rapid decrease in the concentration of organic matter (COD). Assuming mononuclear speciation of aluminum, the aluminate ion is the dominant aqueous species at pHs greater than or equal to 9.8. However, the negatively charged emulsion cannot be destabilized by this ion. In addition, the experimental data of Zeta potential indicated that destabilization occurred in pH values between 9.7 and 10.9. For these pHs the anion $\text{Al}(\text{OH})_4^-$ already predominates so that coagulation by charge neutralization seems unlikely. According to Holt (2003), the characteristics of the coagulant, a hydrolyzed metal cation at low concentrations, restricts the possible mechanisms of coagulation. Therefore, neither the compression of the electric double layer nor the formation of bridges, which normally occurs with the addition of a high molecular weight polymer, is possible. Thus, the nature of electrocoagulation limits the mechanisms of coagulation

to a sorption-type mechanism without precipitation or to a sweep mechanism in case of precipitation. As it appears that coagulation by charge neutralization seems unlikely, there only remains the possibility of a sweep coagulation mechanism. In electrocoagulation, the hydroxyl ions are continuously released at the cathode as the water is reduced and the aluminum cations diffuse from the surface of the anodes to the bulk of the solution, with the possible formation of polynuclear aqueous species. As the system ages, more complex polynuclear species are formed. Hence, the thermodynamic analysis was again applied to consider the influence of more complex aluminum species and to investigate the behavior and interactions of the coagulant and its hydrolyzed metal ions with the pollutant. Table 1 presents the aluminum species considered in the analysis.

Aluminum hydrolysis occurs very rapidly forming all monomeric species and possibly aluminum hydroxide. The aluminum-water speciation changes as the solution ages with larger species typically formed at lower rates. The results when the oligomers (polynuclear species

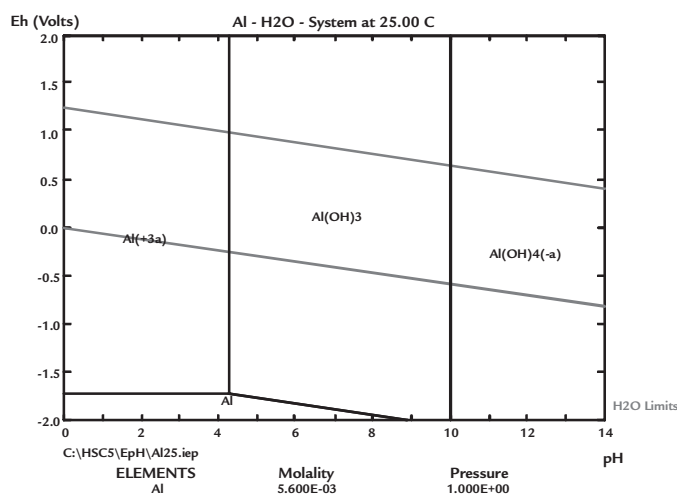


Figure 3
Eh-pH diagram for the reactive stage of electrocoagulation.

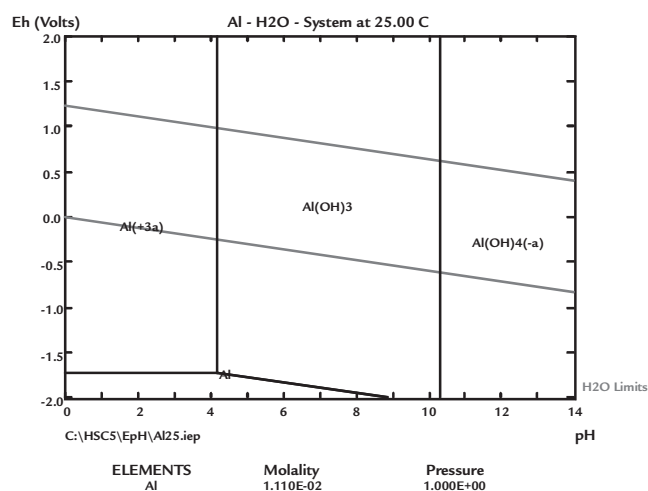


Figure 4
Eh-pH diagram for the stabilization stage of electrocoagulation.

Group	Species
Water	$H^{(+a)}$, $OH^{(-a)}$, $H_2O(l)$
Monomeric aluminum	$Al^{(+3a)}$, $AlOH^{(+2a)}$, $Al(OH)_2^{(+a)}$, $Al(OH)_3^{(a)}$, $Al(OH)_4^{(-a)}$
Dimeric aluminum	$Al_2(OH)_2^{(+4a)}$
Trimeric aluminum	$Al_3(OH)_4^{(+5a)}$
Aluminum 13	$Al_{13}O_4(OH)_{24}^{(+7a)}$
Aluminum hydroxide	$Al(OH)_3$
Aluminum oxide	Al_2O_3

Table 1
Aluminum species considered
in the thermodynamic analysis.

included) and aluminum oxide were taken into account are depicted in Figures 5 to 7. These figures show the formation of the positively charged trimeric species $Al_3(OH)_4^{5+}$. The partial production of this highly charged ion may be responsible for the destabilization of the emulsion and its coagulation by a mechanism of charge neutralization. Independent of the exact speciation of aluminum in solution, the overlap that occurs between the values of pH and Zeta potential at the beginning of the reactive stage strongly suggests that some kind of sorption mechanism is the primary mechanism of coagulation in this stage, more likely charge neutralization.

The analysis suggests that the pre-dominant species during the reactive stage

are the aluminum hydroxide (assuming mononuclear aluminum speciation) and the trimeric positively charged species $Al_3(OH)_4^{5+}$ (for polynuclear aluminum speciation). The surface of the hydroxides may be positively or negatively charged by adsorption of ions from the solution. Thus, it is possible that the destabilization of the emulsion was caused by charge neutralization jointly conducted by polynuclear species and positively charged aluminum hydroxide particles. This means that charge neutralization would be the primary mechanism of coagulation by sorption most likely during the reactive stage. It is also proposed the formation of hydroxide and/or aluminum oxide precipitates during the stabilization

stage, which suggests a gradual change of the dominant oil removal mechanism to sweep flocculation.

It should be pointed out that these considerations about the mechanisms of coagulation are essentially valid for an electric current equal to 2.0 A, which was used in most of the experiments. It is essential to provide the necessary time for solution aging thus favoring the formation of complex aluminum cations, especially $Al_3(OH)_4^{5+}$. This is not possible when using high electrical currents. The analysis was based on the assumption that the variation of COD reduction with time follows the experimentally observed “inverted S” shape. Otherwise, i.e., if the current

Figure 5
Eh-pH diagram for the inertia stage
considering polynuclear species.

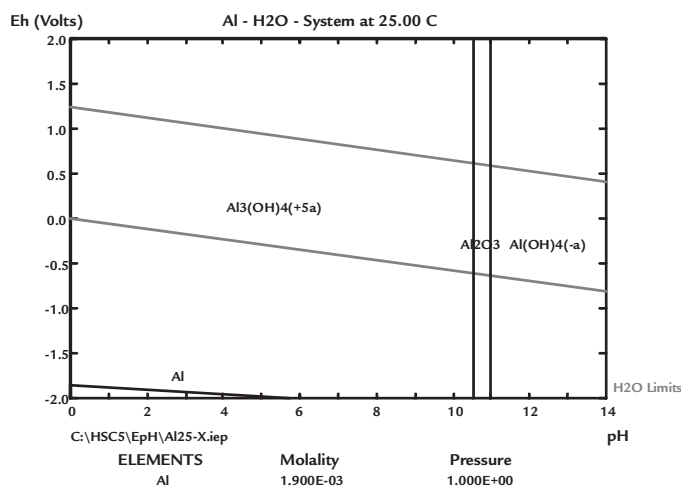
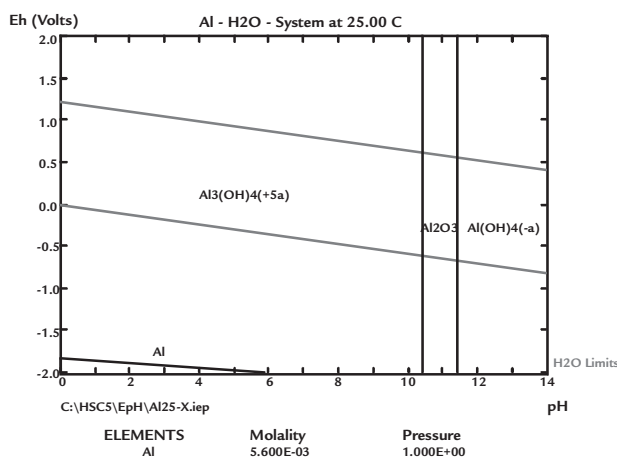


Figure 6
Eh-pH diagram for the reactive stage
considering polynuclear species.



density is high enough, there would not be time for the proper aging of the solution and formation of polynuclear cationic species. In such case, the most likely destabilization mechanism is sweep coagulation. Therefore, the current density plays a major role in the mechanism of emulsion destabilization.

The particles are expected to aggregate during electrocoagulation. The faster oil removals occurred during the reactive stage regardless of the pollutant concentration. To ensure effective aggregation, the particles must bind and their interactions are very important. The literature discusses several aggregation mechanisms depending on the type of particle-particle interaction. Cañizares et al. (2008) reported that when the droplets are charged the binding of more than one droplet to a charged destabilizing agent (flocculation bridging) should be the primary destabilization mechanism. However, it is clear that this mechanism would not be upheld by the monomeric species. Accordingly, only the polymeric

hydroxy-aluminum cations or charged aluminum hydroxide precipitates could cause the emulsion break-up. Due to the small size of the cations in comparison to the size of a droplet, ionic monomeric aluminum species could only act on a droplet. On the other hand, the size of the polymeric ions and especially that of the precipitate could cause the association of more than one droplet with such a coagulant species. In this case, the organic matter content in the bound droplets could be put sufficiently close to promote coalescence. Still according to Cañizares et al. (2008), an excess of coagulant concentration could decrease the efficiency of the electrocoagulation process. This may be explained by the fact that with increasing the number of charged aluminum hydroxide particles, the possibility that more than one oil droplet be connected to the same particle (which is the first stage necessary to promote coalescence of oil droplets) diminishes. Alternatively, an increase on the average size of the particles and then

a decrease on the efficiency of aluminum usage (less surface area of particles per unit mass of dissolved aluminum) are more feasible.

A sulfate medium (Na_2SO_4 as electrolyte) enhances the formation of precipitates rather than the formation of hydroxy-polymeric ions (since the solubility of aluminum is higher in NaCl than in Na_2SO_4). In sulfate medium, 70% of aluminum is present as amorphous aluminum hydroxide precipitates, while in chloride medium this percentage is around 40%. Thus, the remaining aluminum should be mostly in the form of hydroxy-polymeric cations meaning that the active sites that promote coalescence would be larger in the chloride medium (aluminum is more efficiently used). The aluminum hydroxide which is not on the surface of the particles would not be effective in terms of treatment and due to its smaller size and more efficient aluminum content it would be expected that the polymeric ions had better efficiencies.

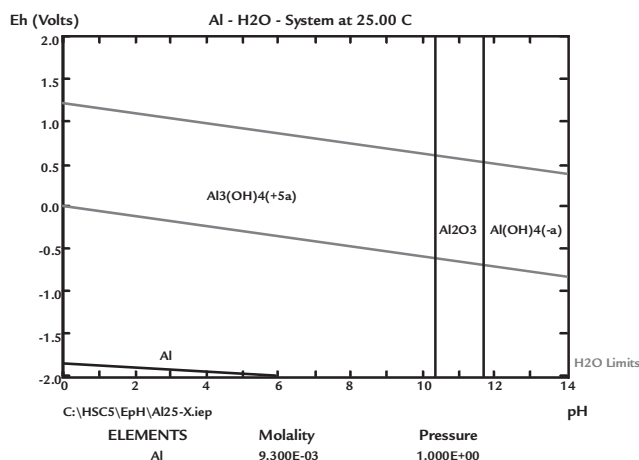


Figure 7
Eh-pH diagram for the stabilization stage considering polynuclear species.

4. Conclusions

Three ranges of aluminum concentrations were observed in the curves of COD reduction and organic matter removal as a function of time. These ranges correspond to the stages of inertia ($[\text{Al}^{3+}] < 0.1 \text{ kg.m}^{-3}$), reactive ($0.1 \text{ kg.m}^{-3} < [\text{Al}^{3+}] < 0.2 \text{ kg.m}^{-3}$) and stabilization ($[\text{Al}^{3+}] > 0.2 \text{ kg.m}^{-3}$).

The thermodynamic analysis suggests that the predominant species during the reactive stage was aluminum hydroxide, for mononuclear aluminum speciation, and the trimeric positively charged

species $\text{Al}_3(\text{OH})_4^{5+}$, for polynuclear speciation. The surface of the hydroxides may be positively or negatively charged by adsorption of ions from the solution. It is possible that the destabilization of the emulsion was obtained by charge neutralization jointly conducted by polynuclear species and positively charged aluminum hydroxide particles. Therefore, charge neutralization would be the primary mechanism of coagulation by sorption most likely during the reactive stage. The analysis also proposes the formation of

hydroxide and/or aluminum oxide precipitates during the stabilization stage, which hints at a gradual change of the dominant oil removal mechanism to sweep flocculation. The current density plays a major role on the mechanism of emulsion destabilization. The above considerations about the coagulation mechanisms are essentially valid for an electric current equal to 2.0 A, which was used in most of the experiments. For higher current densities the most likely destabilization mechanism was sweep coagulation.

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