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Selective removal of dodecyl sulfate during electrolysis with aluminum electrodes

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ABSTRACT

Electrolyses with aluminum electrodes were performed to control the removal of dodecyl sulfate (DS) from aqueous solutions. When electrolyses were conducted in 0.1 M HCl solution and in the presence of 6.9–13.8 mmol L^{-1} of DS the pH increased and electrogenerated Al^{3+} ions and DS anion led to the formation of a precipitate after an induction period. The abatement of DS anion was about 80% at a concentration of 13.8 mmol L^{-1}, when the molar ratio DS/Al was near 3. For electrolyses carried out in 0.1 M NaCl solution, the pH increased from 5 to 9.4 and an alumina precipitate was formed. The removal of DS anion was less efficient than in acid solution. The abatement did not depend upon the DS concentration in the range 6.9–13.8 mmol L^{-1} and it slightly increased until 20% with the electrolysis time. These results were in agreement with a DS anion adsorption on electro-generated alumina which was investigated. The adsorption capacity was found at 0.865 mmol g^{-1} of alumina. This selective removal of DS anion, thanks to a pH control, was applied in the recycling of a deinking wastewater.

Keywords: Surfactant; Dodecyl sulfate; Electrocoagulation; Electrolysis; Aluminum

1. Introduction

Surfactants are chemicals which decrease the surface tension of a liquid, or lower the interfacial tension between two liquids or between a liquid and a solid. Thanks to this property, surfactants constitute a very important group of compounds in modern life. They are useful in a large variety of usual products like soaps, detergents for household cleaning or in pharmaceuticals and personal care products. They are also found in industrial applications, in many fields like paints, cosmetics, pharmaceuticals, agrochemicals, paper coatings, and environmental remediation [1]. Whatever their structures, surfactants contain hydrophilic groups which help their dissolution in water. There are four classes of surfactants based on the ionic charge of the hydrophilic part: cationic, anionic, amphoteric, and non-ionic. All are soluble in water, and since they are widely used, a large part of them ends up in wastewaters where they are emerging pollutants [2]. Surfactants are harmful to human beings, fishes, and vegetations and they generate foam

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on rivers and reduce the water quality. So, surfactants in effluents constitute a new kind of pollutants which needs the research of treatments aiming their removal or destruction [3–11]. Many techniques have been investigated: activated sludge treatment [3], sonochemical degradation [4], advanced oxidation [5], membrane separation [6], coagulation [7], and adsorption [8–12]. The adsorption process seems to be a good method for removing surfactants, especially in the case of low concentrations. Many adsorbents have been used: activated carbon [9], alumina [10,11], and sand [12]. Electrochemical treatments are also applied to wastewaters which contain surfactants [13–15]. Despite its efficiency in various pollutant removals [16], electrocoagulation has rarely been used for surfactant treatments [17,18]. This study presents the first use of electrolysis with aluminum anode in the treatment of synthetic solutions that contain sodium dodecyl sulfate (SDS) which is also known as sodium lauryl sulfate. This treatment, also known as electrocoagulation, offers the advantage of allowing coagulation and separation of pollutants without the use of chemicals.

SDS is a synthetic surfactant widely used in commercial detergent formulations. SDS is not very toxic for humans but its toxicity has been determined against aquatic organisms [19–21]. Treatments for its removal from wastewaters have been investigated [4,10,12,22]. Removal of SDS from aqueous media occurs by coagulation [22], oxidation [23] and mainly by adsorption on various sorbents and at different pH [10,12]. Peroxi-electrocoagulation oxidation process is efficient in the removal of SDS. This treatment uses oxidation with hydrogen peroxide during electrolysis with soluble iron anode. The removal yield reaches 80% [23].

Aqueous solutions containing significant amounts of SDS were treated by electrolysis using soluble aluminum electrodes looking for a selective removal of the surfactant or an inefficient process. Each result could be of interest in a recycling process. A control of the pH allowed a selective removal of dodecyl sulfate (DS) anion. The low adsorption of DS anion was checked on electro-generated alumina. A recycling of deinking effluent is presented as an example of application of a selective removal of DS by electrocoagulation.

2. Materials and methods

2.1. Chemicals

SDS was a Fluka reagent (98%) Methylene blue (MB) (99%) and chloroform (99%) were analytical reagent grade and were supplied from Riedel de Haën and Aldrich, respectively. All other chemical reagents used were commercial and used without further purification. All aqueous solutions were prepared by dissolution in de-ionized water.

2.2. Electrolysis

All electrolyses were carried out at a constant current provided by a Micro Lab 300 V–1 A generator. Four or five identical electrochemical cells were connected in series. Cells were made of 0.4 L beaker which contained 0.25 L of magnetically agitated solution. Cathodes and anodes were made of industrial aluminum. The working surface of one side of electrodes was 15 cm^2 (3×5 cm). Electrolysis were generally carried out with constant current of 0.1 or 0.2 A, corresponding to current density of 66.6 or 133.3 $A\,m^{-2}$, respectively. Before experiments, the electrodes were etched in 2 M NaOH solution during 5 min and then rinsed with de-ionized water, dried in an oven at 100° C and finally weighed. During electrolysis, the current was periodically switched off in order to take samples of solution and to make measurements. Turbidity was measured with a HACH 2100P apparatus. The pH measurements were carried out with a glass electrode and a Metrohm 827 pH meter. At the end of electrolysis, the solutions were filtered. The solid phases were washed with de-ionized water, dried in an oven at 100°C and finally weighed before their analyses.

2.3. Analysis

Concentrations of DS in solution were determined thanks to the formation of its complex with MB which was extracted with chloroform, following a reported procedure [24]. The chloroform extracts were dried with Na_2SO_4 and then analyzed at 653 nm, with a spectrophotometer Lambda 35 PerkinElmer cells.

The solid phases that were separated after electrolysis have been analyzed. IR spectroscopy was performed with a Shimadzu FT–IR spectrophotometer after dispersion in KBr annealed at 100°C. Thermogravimetric analysis (TGA) was carried out in air atmosphere using the Shimadzu DTA/TGA50 with a heating rate of 6°C mn^{-1}.

Powder X-ray diffraction (XRD) patterns were collected with a INEL XRG 3,500 diffractometer using Cu Kα (1.540560 Å) at 30 kV and 30 mA with an angle range 2θ between 5° and 120° and step length of 0.02° (2θ).

2.4. Adsorption on electro-generated alumina

An electro-generated alumina sample was prepared by electrolysis with aluminum electrodes in

0.25 L of 0.1 M NaCl. The current was maintained constant at 1 A during five hours. At the end of electrolysis, the solution was filtered and the solid was washed with de-ionized water, and then dried in an oven at 100˚C, leading to about 6 g of a white powder. The specific area was determined by the BET method giving a value of 217 $m^2 g^{-1}$ using a standard instrument AS1 KR/MP.

The point of zero charge (pH_{PZC}) was determined by a potentiometric titration method carried out in 0.01 M $NaNO_3$ [25] with use of pH meter Metrohm 827. 50 mL of alumina suspensions were titrated with 0.1 M HNO_3 or 0.1 M NaOH. The charge density ($C\,m^{-2}$) on the surface was calculated at each pH value using Eq. (1) where F is the Faraday constant (96,480 $C\,mol^{-1}$), A is the specific surface of solid ($m^2 g^{-1}$), ρ is the concentration of the suspension ($g\,L^{-1}$), C_a and C_b are the concentration of acid or base added to the suspension or blank.

$$\sigma = (F/A\rho)[(C_a - C_b)_{susp} - (C_a - C_b)_{blanck}] \quad (1)$$

2.5. Recycling of deinking effluents

The deinking experiments were carried out with paper of newspaper which contained colored and black inks. Paper was treated at the dose of 15 $g\,L^{-1}$ in a water solution of SDS at 5 $g\,L^{-1}$, at 60˚C during 1 h. After filtration of the paper pulp, the residual solution was treated by coagulation or electrocoagulation. $AlCl_3{\cdot}6H_2O$ was used as coagulant at the dose of 1.4 $g\,L^{-1}$. The solution was agitated during 1 h before filtration. The electrocoagulation was carried out with aluminum electrodes at a constant current of 0.1 A. To increase the conductivity, NaCl was added at 0.1 $mol\,L^{-1}$. The duration of the electrolysis was chosen to dissolve a calculated aluminum weight equivalent to the amount of coagulant. After separation of the solids formed during the coagulation or the electrocoagulation, the residual solutions were tested in a second deinking experiment.

3. Results and discussion

3.1. Choice of the experimental conditions

The experiments have been performed at room temperature with four or five electrochemical cells connected in series. One cell was used for a blank experiment. SDS was used at different concentrations above its critical micellar concentrations which are at 8.3 mM in water and 1.8 mM in 0.1 M NaCl [26].

Electrocoagulations are generally carried out in the presence of chloride or nitrate ions. During preliminary experiments, the foaming which was observed in the presence of nitrate ions was greater than in the presence of chloride ions. So, all the electrolyses were conducted in 0.1 M HCl or 0.1 M NaCl. Hydrogen evolution at the cathode was involved in the foam formation. To reduce the foam quantity, the electrolysis current was controlled at 0.2 and 0.1 A in HCl and NaCl solutions, respectively. In all electrolyses, the experimental weight loss of aluminum electrodes was greater than the value calculated by the Faraday law. This observation is attributed to chemical dissolution beyond electro-dissolution of the aluminum electrodes [27]. The electrochemical reactions Eqs. (2)–(4) make the solution more acid and alkaline in the vicinity of the anode or cathode surface, respectively. Since aluminum is known to be soluble in both acidic and alkaline media, the cathode corrosion occurs during the electrolyses [28]. This explains the unexpected weight loss of the cathode.

$$2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O \text{ (in acid solution)} \quad (2)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \text{ (in neutral solution)} \quad (3)$$

$$Al \rightarrow Al^{3+} + 3e^- \quad (4)$$

3.2. Electrolysis in acid solution

Electrolyses were performed in 0.1 M HCl, at current intensity of 0.2 A with SDS concentrations of 26.6, 41.1 and 53.2 mM. The voltage between the electrodes increased from 10 to 30 V for 120 min of electrolysis which probably results from a decrease in the conductivity of the electrolyte. Indeed, the protons were consumed by reduction on the cathode Eq. (2) while Al^{3+} arose from the anode Eq. (4). The conductivity decrease was due to a mobility of Al^{3+} which is lower than the one of H^+ [29].

The variations of pH and turbidity during the electrolyses are presented in Fig. 1. In the absence of SDS, the pH increased from 1.25 to 2.28. This pH increase was in agreement with the consumption of protons in the cathode reduction Eq. (2). As expected for an acid solution where Al^{3+} ions are soluble, the precipitation of alumina did not occur and the turbidity was rather weak at 71 NTU. On the other hand, in the presence of SDS, a great increase in the turbidity was observed. It exceeded rapidly 1,000 NTU, while the pH remained acid. This observation proves that the formation of a solid occurred with the involvement of Al^{3+} and DS anion. This solid is named Al-DS precipitate in this paper.

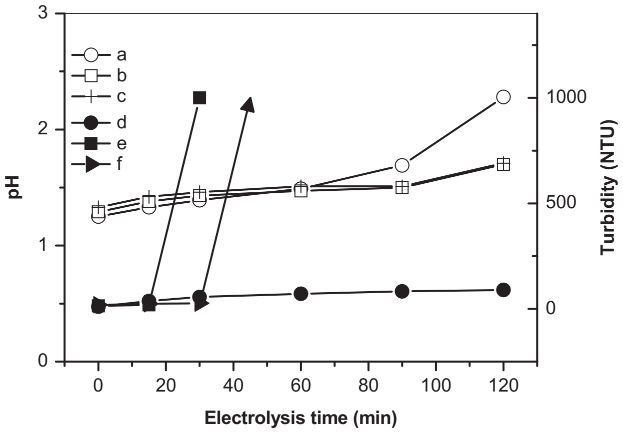

Fig. 1. Variation of pH (curves a–c) and turbidity (NTU) (curves d–f) during the electrolysis in 0.1 M HCl solution (current 0.2 A; current density 133.3 A m^{-2}; DS concentrations: a and d: 0; b and e: 26.6 mM; c and f: 53.2 mM).

After 30 min of electrolysis and in the presence of 6.65 mmol of SDS, corresponding to an initial concentration of SDS of 26.6 mM, the turbidity was around 1,000 NTU, while in the presence of 13.3 mmol, corresponding to a SDS concentration of 53.2 mM, the electrolyzed solution remained quite limpid with a turbidity of 27 NTU. At 30 min, the formation of an Al–DS precipitate occurred notably when the amount of Al^{3+} arising from the anode was 1.24 for 6.65 mmol of DS and the molar ratio SDS/Al^{3+} was at 5.36. At 30 min, for a 53.2 mM SDS solution the molar ratio SDS/Al^{3+} was at 10.7 and any precipitation did not occur.

The behavior of the ternary system which contains SDS and Al^{3+} in water has been investigated in recent years [30–32]. In this system, Al^{3+} neutralizes the electrostatic repulsion between negatively charged micelles which flocculate and afford sub-stoichiometric Al–SDS aggregates easily filterable. These aggregates can adsorb anionic organic pollutants from waste waters allowing their removal. This separation process is named Adsorptive Micellar Flocculation (AMF) [33]. The main observations about the formation of Al–DS precipitate were in agreement with the occurrence of a precipitation when the molar ratio SDS/Al^{3+} was lower than 6.7/1 [32]. The absence of precipitation when the molar ratio SDS/Al^{3+} was at 10.7 is also in agreement with the fact that an addition of aluminum salt allows the dissolution of the Al–DS precipitate [32].

Despite the extensive investigation of the system SDS and Al^{3+} the composition of the Al–DS precipitate is not clearly established. This may be due to the existence of polynuclear hydrolytic complexes of Al(III) which can be involved in ion pairing with DS anion. In the pH range of electrolyses in 0.1 M HCl, Al^{3+} was probably the major species, and a stepwise formation of intermediate species $Al(DS)^{2+}$ and $Al(DS)_2{}^{+}$ was not excluded before the precipitation of $Al(DS)_3{\cdot}3H_2O$. The literature [34] describes the preparation of aluminum tris (DS) trihydrate Eq. (5) as a white solid obtained after the mixing of aluminum salt and SDS solution. This compound was prepared for comparison with the isolated Al–DS precipitate.

$$Al^{3+} + 3DS^{-} + 3H_2O \rightarrow Al(DS)_3 \cdot 3H_2O \quad (5)$$

In the presence of SDS in solution, the increase in pH was significantly weaker than without SDS (Fig. 1). This observation was in agreement with the hydrolysis of Al–DS ionic intermediates affording protons and solid compounds which contained DS and hydroxyl anions Eqs. (6) and (7).

$$Al(DS)^{2+} + 2H_2O \rightarrow Al(DS)(OH)_2 + 2H^{+} \quad (6)$$

$$Al(DS)_2^{+} + 2H_2O \rightarrow Al(DS)_2(OH) + H^{+} \quad (7)$$

To confirm the formation of Al–DS precipitate during the electrolysis, a new series of experiments were performed and the concentration of DS in solution was determined by analysis. The results are presented in Fig. 2. Whatever the initial concentration, the results follow S-shaped curves. These results did not correspond to a titration behavior involving the formation of Al–DS precipitate. Indeed, the DS concentration decrease occurs for the same times, at about 50 min. This behavior may be due to the onset of precipitation when the molar ratio SDS/Al^{3+} was around or greater than six. At the end of electrolysis,

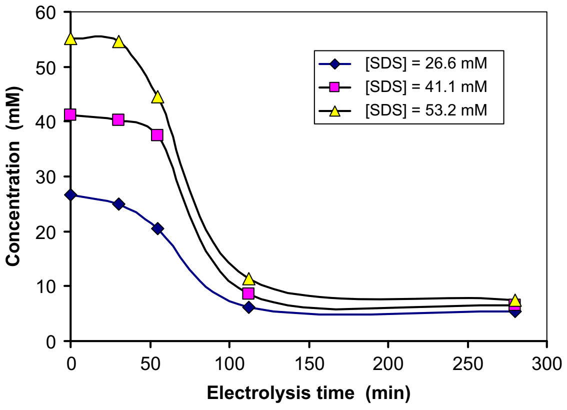

Fig. 2. Variation of DS anion concentrations during constant current electrolysis in 0.1 M HCl. Initial SDS concentrations are given in the insert; solution volume: 0.25 L; electrodes: aluminum; current: 0.2 A; current density 133.3 A m^{-2}.

DS concentrations were notably different from zero, despite the continuous formation of Al^{3+} arising from the anode. In all cases, DS abatements were greater than 90% after 280 min of electrolysis.

3.3. Analysis of Al–DS precipitates

The Al–DS precipitates were isolated after 120 min of electrolysis. In all cases, the calculated molar ratio of SDS/Al^{3+} was lower than 2.7. So, the amount of Al^{3+} was sufficient for the formation of a trivalent compound like $Al(DS)_3{\cdot}3H_2O$. After filtration, and washing, the isolated solid had the appearance of a gel. The dried compounds obtained in the presence of 6.9, 10.4, and 13.8 mmol of SDS weighed 1.30, 2.06, and 2.77 g, respectively, only 65–69% of the theoretical weight of $Al(DS)_3{\cdot}3H_2O$. These low yields may be explained by the formation of Al–DS precipitates which contained one or two DS groups, instead of three.

IR spectra of DS-containing compounds show bands which are characteristic of the DS group [35]. The IR spectrum of the Al–DS precipitate isolated in acid solution was in agreement with the presence of DS group. The vibration bands at 2,920 and 2,850 cm^{-1} were attributed to the asymmetric ν_{as} and symmetric ν_s stretching of $-CH_2-$, respectively. The absorption band at 1,460 cm^{-1} was due to deformation band of $(-CH_2-)$, whereas the weak band at 1,380 cm^{-1} was attributed to $-CH_3$ deformation. Three bands between 1,250 and 950 cm^{-1} were observed, a strong one at 1,235 cm^{-1} corresponded to asymmetric ν_{as} $(-OSO_3-)$ and the bands at 1,160 and 990 cm^{-1} attributed to symmetric ν_s $(-OSO_3-)$.

The heating of 0.5 g of Al–DS precipitates at 500˚C in an oven during 4 h afforded 0.07–0.08 g of Al_2O_3 as a residue. This result shows that the precipitates contained mainly the organic component DS. But this amount was greater than expected (0.029 g) in the hypothesis of Al–DS precipitates which would have the structure $Al(DS)_3{\cdot}3H_2O$. The hypothesis that Al^{3+} ions were involved in the flocculation of Al^{3+}-containing micelles during the electrolysis may explain that the precipitates were sub-stoichiometric compounds.

3.4. Electrolysis in neutral solution

Electrolyses were performed in 0.1 M NaCl and in the presence of SDS with increasing concentrations from 8 to 64 mM. The electrolysis current was controlled at 0.1 A. The results of turbidity and pH measurements are presented in Fig. 3. As it is generally observed, the pH and the turbidity increased concomitantly in the absence of SDS. This behavior is in agreement with a low solubility of Al(III) in this pH range, so the precipitation of alumina occurred at the beginning of the electrolysis.

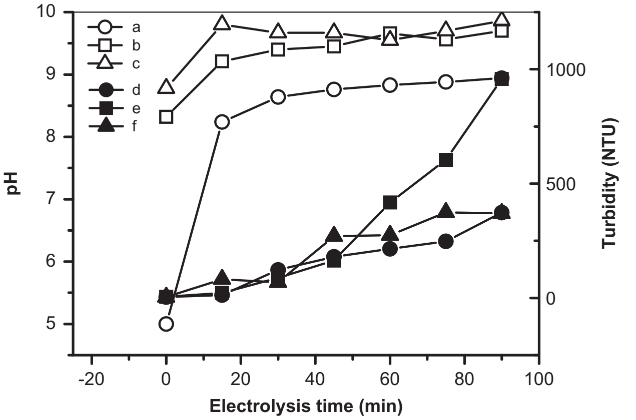

Fig. 3. Variation of pH (curves a–c) and turbidity (NTU) (curves d–f) in 0.1 M NaCl (current 0.1 A; current density 66.6 A m^{-2}; DS concentrations: a and d: 0; b and e: 16 mM; c and f: 64 mM).

In the presence of SDS, the pH was more basic at the start of the electrolysis, due to the alkalinity of DS^-. During the electrolysis, the pH and the turbidity increased. The results show that the turbidity increased with 16 mM SDS and 8 and 32 mM SDS. Results for 8 and 32 mM are not shown in Fig. 3. With the highest concentration, at 64 mM, the turbidity was lower, suggesting that a large concentration of DS favors the dissolution of alumina. From these turbidity results, it is difficult to conclude about the behavior of SDS during the electrolysis. Electrocoagulation in the presence of low concentrations of SDS has already been performed in order to improve the removal of suspended solids [36,37]. But these papers do not give any information about the removal of SDS during electrolysis.

SDS concentrations were determined during the electrolysis. The corresponding results which are gathered in Fig. 4 show that SDS concentrations did not decrease significantly during 90 min. After that, the decrease was more pronounced, and this occurred when the pH was alkaline and favored the dissolution of alumina. This observation suggests that DS anion was involved in a substitution reaction into $Al(OH)_4{}^-$ leading to the precipitation of a compound that contained DS groups Eq. (8). This equation shows that an increase in strong base hydroxide anions would be expected. This is in agreement with the observed pH increase which was greater during the electrolysis in the presence of SDS (Fig. 3).

$$Al(OH)_4^- + DS^- \rightarrow Al(DS)(OH)_2 + 2(OH^-) \qquad (8)$$

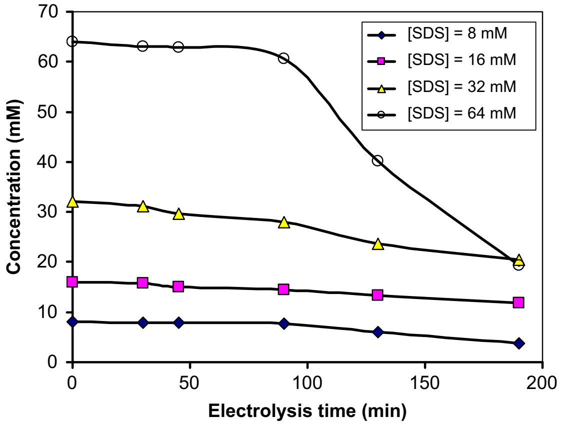

Fig. 4. Variation of SDS concentration during electrolysis in 0.1 M NaCl (current 0.1 A; current density 66.6 A m^{-2}; initial concentrations of SDS are given in the insert).

3.5. Precipitate isolated in neutral solution

After 90 min of electrolysis the formed solids were separated by filtration and the filtrate was again subjected to electrolysis for 100 min. The total weights of isolated dried solids are given in Table 1. These results show that the yield of precipitated solids increases with the SDS content of the solution. This observation proves that DS is incorporated into the precipitate, but the isolated quantities are lower than expected for the formation of $Al(DS)_3$. The nature of the isolated solids is confirmed by their carbonization. The weight loss during carbonization at 500˚C was in agreement with a notable content of DS in the isolated solids (Table 1).

The IR spectra of the solids showed bands which characterized the presence of DS groups in the samples. The data were analogous to those of Al-DS precipitate as described in Section 3.3.

3.6. Adsorption of DS anion on electrosynthesized alumina

During the electrolysis, the electrode reactions are controlled by thermodynamics and kinetics. Oxidation of water or chloride anion is known to involve a large overvoltage which is dependent upon the nature of the electrode. Comparison of the well-known standard potentials leads to the conclusion that the expected oxidation is that of aluminum.

Table 1
Amount of solids obtained after electrolysis in neutral solution (190 min; current 0.1 A; current density 66.6 A m^{-2})

SDS amount (mmol)	Weight of solids (g)	% of residue after heating at 500˚C
0	0.614	66
2	0.969	38
4	1.262	48
8	1.518	48
16	1.460	48

Advanced oxidation uses strong oxidants like ozone or hydroxyl radical for destroying SDS [23]. In KCl solution, the redox potential is measured at−0.2 V/SCE [38]. This negative value proves that the electrolyzed solution of an electrocoagulation is not a strong oxidant. So, the occurrence of an oxidation of DS is excluded during electrolysis with aluminum electrodes.

Since an oxidation of DS is excluded, the DS anion removal occurring during electrolysis in neutral solutions suggests the involvement of an adsorption of DS on electro-generated alumina. The adsorption of DS anion alone or in mixture has already been investigated on various kinds of alumina [7,10,39–41]. It can be concluded that, in addition to precipitation coagulation process, an AMF contributes to the removal of surfactants. Electrosynthesized alumina was prepared by electrolysis in 0.1 M NaCl solution with aluminum electrodes. XRD diagram (Fig. 5) of the electro-synthesized alumina shows that it was a mixture of boehmite AlOOH and bayerite $Al(OH)_3$. Moreover, as shown by their ray widths, boehmite contains nano crystallites. The pH of zero charge of this alumina was found at 8.0 at 20˚C. These characterizations and in particular XRD diagrams show that the electrosynthesized alumina is different from alumina sorbent which were investigated in the presence of SDS [7,10,39–41].

The removal kinetics of DS anion is shown in Fig. 6(a). The experimental data indicated that the adsorption process was very fast at the beginning and then slowed down as equilibrium approached. It was observed that the time required for reaching the equilibrium increased with the increase of initial DS anion concentration. This may be attributed to the increase of columbic repulsion between adsorbed DS group and the DS anions approaching the alumina for adsorption.

Both pseudo-first-order and pseudo-second-order rate models were used to fit the experimental data at pH 6.5 and at 20˚C. The linear forms of the corresponding equations are given by Eqs. (9) and (10) where Q_t is the adsorption amount at a given time and Q_e is the adsorption equilibrium capacity at the terminal experimental time.

$$\ln(Q_e - Q_t) = \ln Q_e + k_1 t \tag{9}$$

$$t/Q_t = 1/(k_2 Q_e^2) + t/Q_e \tag{10}$$

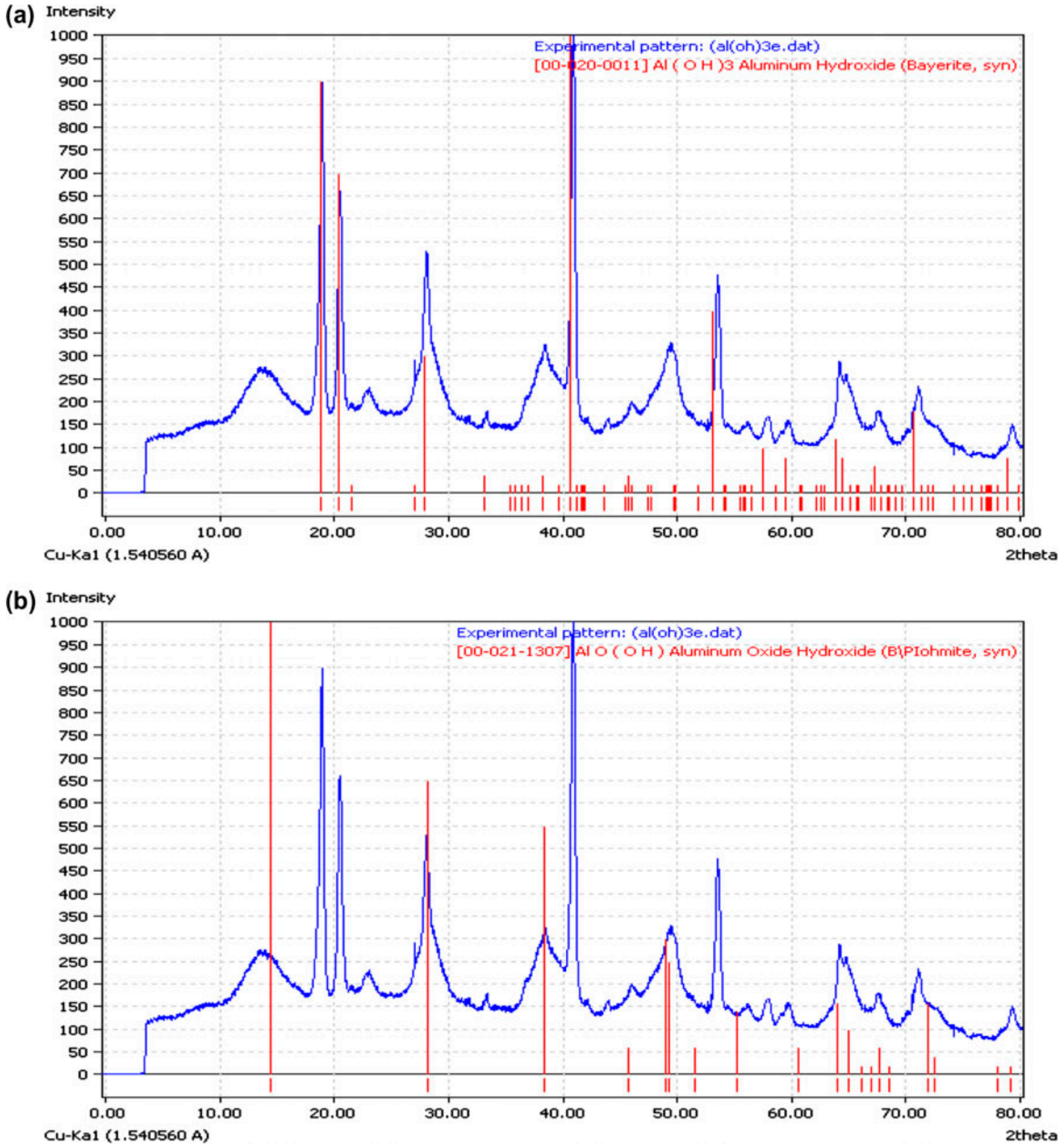

Fig. 5. XRD pattern of the electro-generated alumina isolated after electrolysis in 0.1 M NaCl. (a) Identification of bayerite $Al(OH)_3$ and (b) identification of boehmite AlOOH.

For a pseudo-first-order, the plotting of ln $(Q_e - Q_t)$ vs. time gives a straight line from which the pseudo-first-order rate constant k_1 is obtained from the slope of the plot. For this model, ln $(Q_e - Q_t)$ was plotted vs. t. The linear fit for a DS concentration of 4 and 12 mM gave a correlation coefficient R^2 at 0.821 and 0.983, respectively. These results indicate that the adsorption did not follow this pseudo-first-order equation model.

For a pseudo-second-order equation, the plotting of t/Q_t vs. t leads to a straight line and the values of Q_e and k_2 can be calculated from the slope and intercept of this line. The pseudo-second-order rate model gave perfect fittings to the experimental data (Fig. 6 (b)). The parameters are listed in Table 2. The reaction rate constant was calculated for the pseudo-second-order model and it was found at 0.175 g mmol^{-1} min^{-1} (50.55 g mg^{-1} min^{-1}). These results agree with the

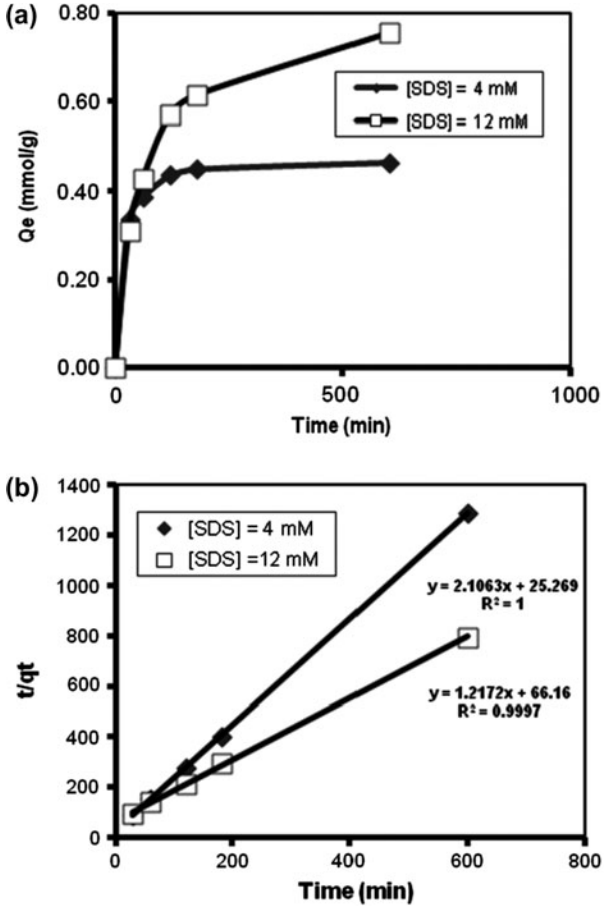

Fig. 6. Adsorption of DS anion on electro-synthesized alumina (0.2 g of alumina in 50 mL; pH 6.45; 20°C). (a) Adsorption kinetics and (b) pseudo-second-order plots for DS anion adsorption.

conclusion of Adak and Pal about the kinetic study SDS adsorption on alumina [39].

Langmuir and Freundlich models are the most common sorption models which are used to fit experimental data. Langmuir and Freundlich models are given by Eqs. (11) and (12), respectively, where K_L is the equilibrium constant of Langmuir, $Q_{\max}$ is the maximal adsorption capacity, K_F is the adsorption capacity of Freundlich and n is the adsorption intensity.

Table 2
Kinetic parameters for adsorption of DS anion at 20°C on electro-synthesized alumina following a pseudo-second-order model

Parameters	4 mM	12 mM
Q_e (mmol g^{-1})	0.474	0.821
K_2 (g mmol^{-1} min^{-1})	0.175	0.022
R^2	1	0.999

$$Q_e = K_L\,Q_{\mathrm{max}}C_e/(1 + K_L C_e) \tag{11}$$

$$Q_e = K_F {C_e}^{1/n} \tag{12}$$

Experimental adsorption curves of DS on electro-synthesized alumina were modeled following models of Langmuir and Freundlich, leading to constant values which are grouped in Table 3.

Adsorption of DS onto alumina is frequently used for the coating of its surface in order to perform co-adsorption of neutral compounds. Adsorption capacities and surface areas of some aluminas are gathered in Table 4 for comparison with electro-synthesized alumina. From these results, it appears that DS adsorption increases with the surface area of alumina. The adsorption performance of electro-generated alumina is situated between those of microsized alumina and nanosized alumina. This observation is in agreement with the structure of the electro-generated alumina which contains nano crystallites of boehmite.

3.7. Recycling of deinking effluent

As an example of recycling of surfactant in a water treatment, few experiments of deinking of newspaper

Table 3
Model parameters for the adsorption of DS anion at 20°C on electrosynthesized alumina

Model	Parameters	Results
Langmuir	$Q_{\max}$ (mmol g^{-1})	0.865
	K_L	0.567
	R^2	0.981
Freundlich	K_F (mmol g^{-1})	0.448
	N	5.090
	R^2	0.968

Table 4
Comparison between various aluminas for SDS adsorption

Alumina adsorbent	Adsorption capacity (mmol g^{-1})	Specific area (m^2 g^{-1})	Reference
Nanosized alumina	1.059	235	[43]
Electrosynthesized alumina	0.860	217	This work
Microsized alumina	0.591	155	[43]
γ-alumina (AlOOH)	0.510	159	[44]
Commercial alumina	0.242	155	[45]
α-alumina (Al(OH)$_3$	0.215	30.2	[46]
α-alumina (Al(OH)$_3$	0.125	8.9	[47]

Table 5
Characteristics of solution after deinking and recycling operations

Successive operations	Turbidity (NTU)	pH	Observations about solution
First deinking	280	9.60	Turbid colored
Electrocoagulation[a]	47	10.20	Colorless, clear,
Second deinking[b]	260	9.80	Turbid
First deinking	280	9.60	Turbid, colored
Coagulation[c]	3	4.03	Colored, clear
Second deinking[d]	4	4.03	Colored, clear

[a] Electrolysis at 0.2 A (current density 133.3 A m^{-2}) during 56 min, after addition of NaCl.

[b] With the filtered solution after electrocoagulation.

[c] Coagulation with 0.35 g of $(AlCl_3)\cdot 6H_2O$ in 0.4 L.

[d] With the filtered solution after coagulation.

were performed. The analysis of patents and publications [42] emphasize the importance of the deinking for use in new production. So, in the recycling of paper, the deinking is an important step which needs a lot of water and surfactants.

The deinking experiments were performed on newspaper which contained black and colored inks. The efficiency of the deinking and the recycling was judged by the variation of color of the paper pulp and by the turbidity of the solutions. The deinking was efficient when it was carried out at 60°C in the presence of SDS at 5 g L^{-1}. After filtration, 0.4 L of the solutions was treated by electrocoagulation at 0.2 A during 56 min, or coagulation with 0.35 g of $(AlCl_3)\cdot 6H_2O$. After filtration, the solutions were used in a new deinking. The results of measurement of pH and turbidity are gathered in Table 5. It appeared that after coagulation, the solution remained colored. In a second deinking, it did not work as well as the solution which had been treated by electrocoagulation. These observations may be due to the fact that (i) the acidification during the coagulation allowed the precipitation of an aluminum DS compounds, (ii) the electro-generated alumina adsorbed the colored ink, and (iii) the electrocoagulation allowed the separation of mater in suspension without removing SDS. These experiments show that the electrocoagulation may be efficient in the selective removal of compounds in a recycling process.

4. Conclusions

Thanks to a control of the solution pH, it is possible to perform by electrolysis with soluble aluminum anode a selective removal of DS from water solution. In acid solution, the ions Al^{3+} arising from the soluble anode and DS anions reacted and afforded a solid with a high content of DS at 229.5 mg g^{-1}. This reaction allows a DS anion removal with abatement greater than 70%. In neutral solution, DS anion abatement was less efficient. The adsorption of DS anion on electrogenerated alumina was investigated. The adsorbed amount calculated in Langmuir model was of 0.86 mmol g^{-1}. The interest of a selective removal of DS anion was illustrated by a recycling experiment. After a first deinking and an electrocoagulation, the treated solution was efficiently used in a second deinking operation.

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