Journal of Hazardous Materials 164 (2009) 353–359

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

# Physicochemical treatments of anionic surfactants wastewater: Effect on aerobic biodegradability

Fathi Aloui, Sonia Kchaou, Sami Sayadi*

*Laboratoire des Bioprocédés, Pôle d'Excellence Régional AUF (PER-LBP), Centre de Biotechnologie de Sfax, BP: 1177, 3018 Sfax, Tunisia*

ARTICLE INFO

*Article history:*
Received 14 February 2008
Received in revised form 7 July 2008
Accepted 5 August 2008
Available online 13 August 2008

*Keywords:*
Biodegradation
*Citrobacter braakii*
Electro-coagulation
Electro-Fenton
Anionic surfactant wastewater

ABSTRACT

The effect of different physicochemical treatments on the aerobic biodegradability of an industrial wastewater resulting from a cosmetic industry has been investigated. This industrial wastewater contains 11423 and 3148 mg $L^{-1}$ of chemical oxygen demand (COD) and anionic surfactants, respectively. The concentration of COD and anionic surfactants were followed throughout the diverse physicochemical treatments and biodegradation experiments. Different pretreatments of this industrial wastewater using chemical flocculation process with lime and aluminium sulphate (alum), and also advanced oxidation process (electro-coagulation (Fe and Al) and electro-Fenton) led to important COD and anionic surfactants removals. The best results were obtained using electro-Fenton process, exceeding 98 and 80% of anionic surfactants and COD removals, respectively. The biological treatment by an isolated strain *Citrobacter braakii* of the surfactant wastewater, as well as the pretreated wastewater by the various physicochemical processes used in this study showed that the best results were obtained with electro-Fenton pretreated wastewater. The characterization of the treated surfactant wastewater by the integrated process (electro-coagulation or electro-Fenton)-biological showed that it respects Tunisian discharge standards.


## 1. Introduction

In Tunisia more than 100 000 $m^3$ per year of surfactants containing wastewater are released. Synthetic surfactants have many industrial applications: washing and cleaning (44%), development of textiles (17%), cosmetic or medicinal products (7%), plastics (5%), foodstuffs (5%), paper (2%), plant health (2%), and metallurgy (7%). Due to their many applications, surfactant can be found at important concentrations in wastewaters producing problematic foams, and inhibiting the activity of certain microorganisms. Their toxicity is not only due to their affinity for the cellular membranes, but also to their capacity to be fixed on proteins causing inhibition of the activity of certain enzymatic proteins.

The presence of a surfactant in a liquid, even in small quantity, can break the surface tension. This property is related to the existence of a hydrophobic part (non-polar) and an absorbent part (polar) in the same molecule. For a biological treatment, the surfactant concentration in the medium cannot exceed 1000 mg $L^{-1}$ due to its toxicity toward microorganisms and foaming in aerated bioreactors [1].

The class of anionic surfactants is very important, it accounts for 60% of the world production. The non-ionic surfactants are less important, approximately 30%, but include a larger variety of chemical species. Amphoteric and cationic surfactants not exceed the 10% [1].

The world production and the use of the chemical compounds such as the surfactants increased enormously. Several of these compounds are biologically not degradable and present a threat to environment [2]. Great number of surfactant agents is not easily biodegradable. Consequently, many physicochemical methods of pretreatment such as the ozonation and other techniques of advanced chemical oxidation were developed to eliminate surfactants [3]. Although effective on the improvement of the biodeterioration of surfactant, ozonation and photocatalytic oxidation are relatively expensive methods. The electrochemical techniques have an important role among advanced technologies of treatment and can cure this problem of pollution.

The principal agents for the degradation of surfactants are the bacteria. A bacterium or a consortium of bacteria for the treatment of wastewaters rich on surfactants must be able to destroy the surfactants properties of the molecule and to use the breakdown products as source of carbon and energy.

Surfactants are toxic for the living microorganisms. They cause the destruction of the function and the structure of the bacterial membranes by increasing their permeability. In the microorganisms, the adsorption of surfactants causes the depolarization of the

* Corresponding author. Tel.: +216 74 874 452; fax: +216 74 874 452.
*E-mail address:* sami.sayadi@cbs.rnrt.tn (S. Sayadi).

0304-3894/$ – see front matter 
doi:10.1016/j.jhazmat.2008.08.009

cellular membranes and decreases consequently the absorption of the nutrients and modifies the release of the substances starting from the cellular metabolism.

The aim of this study is to develop an adequate physicochemical pretreatment step in order to improve the biodegradation of industrial anionic surfactant rich wastewater by decreasing the organic load and the anionic surfactants concentration.

## 2. Materials and methods

### 2.1. Industrial wastewater

The industrial wastewater used in this study was provided from a cosmetic company (JASMINAL, Sfax, Tunisia). The main surfactant used in this factory is the anionic surfactant sodium lauryl ether sulphate (SLES). Some other chemical compounds are also used in the formulation of different cosmetic products, such as: PEG 7 glyceryl cocoate, polyquaternium, Guar hydroxypropyl trimonium, Paraffin oil 30CP, Carbomer and formaldehyde. A sample of wastewater was taken, characterized and then stored at 4 °C. The composition is given in Table 1. Values were the average of three attempts.

### 2.2. Bacterial strain and inoculum preparation

*C. braakii* CTM 50600 [4] culture was used to inoculate the batch cultures. *C. braakii* was grown on basal salt medium (BSM) [5] containing 0.5 g $L^{-1}$ SLES as selective carbon source. The culture parameters were as follow: agitation = 200 rpm; temperature = 30 °C and pH 7.

### 2.3. Cultures

Culture conditions were realized according to Dhouib et al. [5]. Ammonium sulphate was added in the medium for reaching a COD/N ratio of 20 in order to have adequate *C. braakii* growth. The pH of each effluent was adjusted to 7 by the use of NaOH in the case of raw wastewater and with a sulphuric acid solution in the cases of pretreated wastewater. Five percent of *C. braakii* suspension culture was inoculated into the biodegradation tests. The aerobic biological treatment of wastewater using *C. braakii* was developed and studied in sterile conditions in shake-flask cultures consisting of 1 L Erlenmeyer flasks and containing untreated wastewater or pretreated by the different processes developed in this study. The inoculated flasks were continuously agitated on a rotary shaking incubator operating at 200 rpm and 30 °C for 48 h.

### 2.4. Analytical techniques

- pH was analyzed using a Metrohm pH-meter.
- Methylene blue active substance (MBAS) assay used to the estimation of anionic surfactants. This assay was carried out according to Tunisian Norms [6].
- Hyamine colorimetric method was also used for estimating the anionic surfactant in wastewaters when concentrations exceed 40 mg $L^{-1}$.
- COD was estimated as described by Knechtel [7].
- $BOD_5$ was determined by the manometric method with a respirometer (BSB-Controller Model 620 T (WTW)). Two $BOD_5$ tests were realized. One without inoculation (presence of only autochthonous microorganisms), and another with inoculation with the adapted strain *C. braakii*. For this, 1 mL of a *C. braakii* suspension culture was used in 250 mL of adequate diluted samples. A control test was realized in the same conditions without wastewater in order to estimate the $BOD_5$ of the culture suspension and to consider it in calculating $BOD_5$ values.
- Dry matter (DM), total solids (TS), volatile solids (VS), mineral solids (MS), total suspended solids (TSS), volatile suspended solids (VSS) and mineral suspended solids (MSS) were measured as the standard methods for examination of water and wastewater [8].
- The total, mineral and organic nitrogen contents were analyzed as Kjeldahl-N [9].
- The standard method of Soxhlet solid/liquid (organic solids of industrial wastewater/hexane) was used for the dosage of fats.
- Iron concentrations were measured by means of an atomic absorption spectrophotometer.

**Table 1**
Characteristics of the industrial wastewater before and after different treatments (values were the average of three attempts)

| Parameters | Industrial wastewater | Coagulated wastewater (Lime-Alum) | EL-Fe-biological treated effluent | EL-Fenton-biological treated effluent |
|---|---|---|---|---|
| Anionic surfactant (mg $L^{-1}$) | 3148 ± 36 | 1290 ± 16 | 0 | 0 |
| Anionic surfactants removal (%) | – | 53.3 | 100 | 100 |
| pH | 6.77 | 7.35 ± 0.22 | 7.73 ± 0.32 | 8.21 ± 0.28 |
| COD (mg $L^{-1}$) | 11423 ± 460 | 5795 ± 230 | 782 ± 48 | 435 ± 34 |
| COD removal (%) | – | 37.3 | 93.2 | 96.2 |
| Biological oxygen demand | | | | |
| $BOD_5$ (mg $L^{-1}$) | 625 ± 48 | – | – | – |
| $BOD_5$ (mg $L^{-1}$) with addition of *Citrobacter braakii* | 2500 ± 160 | 1220 ± 85 | 312 ± 24 | 180 ± 16 |
| $BOD_5$ removal (%) | – | 51.2 | 87.5 | 92.8 |
| $BOD_5$/COD | 0.22 | 0.21 | 0.40 | 0.41 |
| Dry solids (g $L^{-1}$) | 15 ± 1 | – | – | – |
| Volatile solids (g $L^{-1}$) | 13 ± 1 | – | – | – |
| Mineral solids (g $L^{-1}$) | 2 | – | – | – |
| Fe (mg $L^{-1}$) | – | – | 42 | 58 |
| Total suspended solids (mg $L^{-1}$) | 250 ± 18 | – | 50 ± 4 | 35 ± 3 |
| Volatile suspended solids (mg $L^{-1}$) | 100 ± 8 | – | – | – |
| Mineral suspended solids (mg $L^{-1}$) | 150 | – | – | –– |
| Fats (mg $L^{-1}$) | 600 ± 46 | – | 18 ± 2 | 25 ± 2 |
| Total nitrogen (mg $L^{-1}$) | 113 ± 7 | – | 50 ± 4 | 35 ± 3 |
| Mineral nitrogen (mg $L^{-1}$) | 0 | – | –– | – |
| Organic nitrogen (mg $L^{-1}$) | 113 ± 7 | – | – | – |

*2.5. Coagulation assays of the industrial effluent*

Flocculation and coagulation are mainly used, when the application of sedimentation is not feasible, due to the presence of extremely fine particles or globules, which do not possess a significant settling rate, because the phases do not appreciably differ in density from the parent liquid [10].

Different assays of coagulation were realized using the lime and aluminium sulphate (alum) in order to define the best conditions for the treatment of the industrial effluent (data not shown). This study was undertaken by the use of the "Numerical Flocculator 10408, Fisher Bioblock Scientific". Experiments were conducted at room temperature (23–26 °C). Lime and alum doses range between 0.5–2 and 2–4 g $L^{-1}$, respectively. The best conditions were selected for the highest COD and surfactants removals, good and fast decantation and also an adequate pH around 7 for a further biological treatment. The optimum conditions used in this work to treat the industrial wastewater are as follows:

- stirring speed: 70 rpm;
- lime concentration: 1 g $L^{-1}$;
- aluminium sulphate: 3 g $L^{-1}$;
- reactions time: 15 min after lime addition, and 15 min after aluminium sulphate addition;
- settling time: 4 h.

*2.6. Electro-Fenton and electro-coagulation treatment*

For the electro-Fenton tests, experiments were carried out in a 0.25 L glass reactor. The aqueous solution of reactants was homogenized by magnetic agitation to avoid concentration gradients. The electro-Fenton reactor was formed by one pair of anodic and cathodic electrodes (cast iron plates) which were positioned approximately 1.5 cm apart from each other and were dipped in the effluent. The total effective surface area of electrodes was 0.2 $dm^2$. The current input was supplied by a "CONVERGY power supply". In each run, approximately 0.2 L of the industrial wastewater was placed in the electrolytic cell. The pH of the solution was adjusted to 4. $H_2O_2$ was added to the electrolytic cell before the electrical current was turned on. A batch study was conducted to optimise $H_2O_2$ concentration. This parameter was examined in the range of 0–1.5 g $L^{-1}$. The optimum $H_2O_2$ concentration was found to be 1 g $L^{-1}$.

In the electrochemical process, the material of electrodes is essential for the reactions. Iron and aluminium electrodes were chosen for this study, because they are cheap and easy to produce. Electro-coagulation of the industrial effluent was carried out in the same glass reactor as for the electro-Fenton without stirring. This electrolysis process lasted 1 h at different current densities. The optimum pH for $Al_3{}^+$ and $Fe_3{}^+$ for wastewater coagulation are 6–7.4 and higher than 5, respectively. The pH of the industrial wastewater is equal to 6.77. For this, EL-Fe and El-Al assays were realized without pH adjustment.

## 3. Results and discussion

*3.1. Characteristics of the industrial wastewater*

The characteristics and average composition of the industrial wastewater are given in Table 1. The COD value equal to 11423 mg $L^{-1}$ proves the high organic load of the industrial wastewater. A large part of the organic matter is constituted of anionic surfactants reaching a concentration of about 3148 mg $L^{-1}$. The pH of the wastewater is around the neutrality. The $BOD_5$ of the surfactant wastewater is relatively low as a result of its low biodegradability. The inoculation with *C. braakii* increases the $BOD_5$ but the ratio $BOD_5$/COD remains low. This strain is a powerful bacterial isolate able to degrade wide range of anionic surfactants as reported in a previous work [5] and consequently increases $BOD_5$.

Anionic surfactants, COD and $BOD_5$ of the industrial wastewater largely exceed Tunisian water standards which are 5, 1000, and 400 mg $L^{-1}$, respectively.

As can be seen in this Table 1, the total Kjeldahl nitrogen (TKN) concentration was very low. Consequently, in biological treatment manipulations, ammonium sulphate was added in the medium for reaching a COD/N ratio of 20 in order to have adequate *C. braakii* growth.

*3.2. Coagulation of the surfactant wastewater using lime and aluminium sulphate*

Recently, there has been increasing interest in the use of chemical coagulations and electrochemical methods for the treatment of recalcitrant toxic wastes. The cost of chemical coagulation is low and economic for the treatment of wastewaters [11].

Coagulation process is largely common in wastewaters treatments and knowing for its possibilities of destabilizing and of incorporating colloids [12]. In a conventional wastewater treatment, the coagulants such as aluminium chloride, ferrous sulphate, aluminium sulphate, ferric chloride and hydrated lime are most largely used in reason of their effectiveness, low cost, easy to handle and availability. The aluminium coagulants are more effective at lower temperatures and a broader range of pH.

Coagulation tests were carried out using lime and alum. In the optimal conditions, COD and anionic surfactants removals, as well as pH and $BOD_5$ were determined. Important removals of anionic surfactants and COD were obtained as can be seen in Table 1. During addition of lime there was a raise in pH but after addition of aluminium sulphate, a decrease in pH occurred. Since highly alkaline and acidic conditions are harmful for the biological growth, the combined dose of aluminium sulphate and lime was optimized considering the pH of the effluent. The final pH of the pretreated industrial wastewater (around the neutrality) promotes a biological treatment. In contrast, the products of chemical coagulation by combined treatment of lime followed by aluminium sulphate at optimum dosage was not favourable for biological treatment as the $BOD_5$/COD ratio of effluent was within the value of 0.21.

*3.3. Pretreatment of the industrial effluent by electro-coagulation (EC)*

Tests of pretreatment of the industrial effluent by EC were carried out with the same sample of the industrial wastewater (Table 1).

The mechanism of EC is dependent on the chemistry of the aqueous medium, especially conductivity. In addition, other characteristics such as pH, particle size, and chemical constituent concentrations will also influence the EC process. The efficiencies of the electrochemical processes depend on the current density and the nature of the anions contained in the waste [12]. In this study two electrode types were tested (aluminium and iron).

*3.3.1. Electro-coagulation of the surfactant wastewater using aluminium electrodes (EL-Al)*

The oxidation of the industrial wastewater by EL-AL showed an increase in the pH. Maximum values of pH were obtained with a current density of 1.25 A $dm^{-2}$. Indeed, with this current density the pH reached the value of 10.38 after 60 min (data not shown). This treatment allowed important COD and anionic surfactants

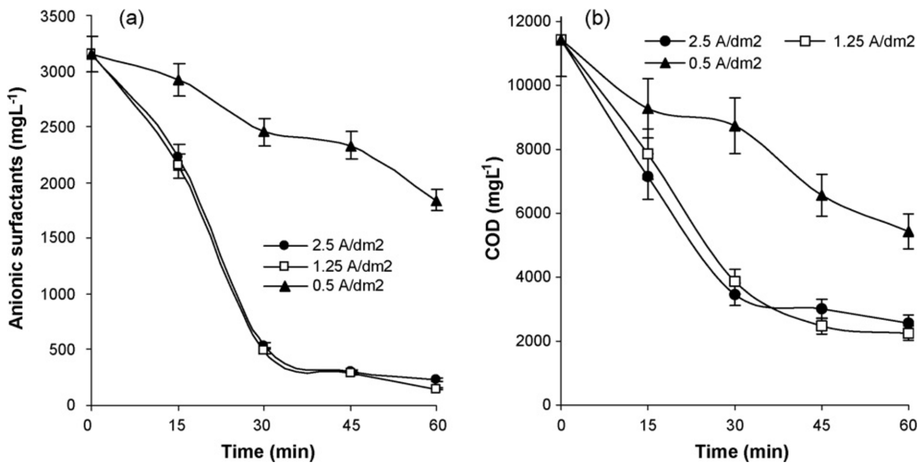


**Fig. 1.** The evolution of (a) anionic surfactants concentrations and (b) COD during the electro-flocculation of the industrial wastewater using Al electrodes at different current densities. (●) 2.5 A $dm^{-2}$, (□) 1.25 A $dm^{-2}$, and (▲) 0.5 A $dm^{-2}$. Data points are the average of three replicates, and the error bars shown are the standard deviation.

removals with the current densities of 1.25 and 2.5 A $dm^{-2}$ (Fig. 1). The application of a current density of 0.5 A $dm^{-2}$ led to approximately 50% of COD and surfactants removals after 1 h of treatment.

Fig. 1a shows an important decrease of anionic surfactants in the case of a current density of 2.5 A $dm^{-2}$. In fact, this treatment for 1 h allowed a reduction of anionic surfactants in the industrial wastewater from 3148 to 140 mg $L^{-1}$. Anionic surfactants removals are less important in the cases of 1.25 and 0.5 A $dm^{-2}$ current densities. For this treatment, COD removal is also important, especially when the current density is equal to 2.5 A $dm^{-2}$ (Fig. 1b).

### *3.3.2. Electro-coagulation of the industrial wastewater using iron electrodes (EL-Fe)*

Iron leading oxidation in an electrolytic system produces iron hydroxide, $Fe(OH)_n$, where $n = 2$ or 3. The $Fe(OH)_n$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation.

The treatment of the industrial wastewater by EL-Fe showed an increase in the pH. Maximum values of pH were obtained with a current density of 2.5 A $dm^{-2}$. In fact, using this current density, the pH reached the value of 12.52 after 60 min (data not shown). El-Fe treatment allowed COD and anionic surfactants removals of 78.1 and 98.5%, respectively, with the current density of 2.5 A $dm^{-2}$ (Fig. 2). On the other hand, the application of a current density of 0.5 A $dm^{-2}$ leads only to 30.3 and 34.6% of COD and anionic surfactants respectively after 1 h of treatment.

EL-Fe treatment for 1 h at a current density of 2.5 A $dm^{-2}$ allowed a reduction of anionic surfactants in the industrial wastewater from 3148 to 46 mg $L^{-1}$. The elimination of surfactants is less important in the cases of 1.25 and 0.5 A $dm^{-2}$. Also, the COD of the EL-Fe treated industrial wastewater was about 2500 mg $L^{-1}$ using the current density of 2.5 A $dm^{-2}$. However, the COD was about 6931 and 7962 mg $L^{-1}$ in the cases of the treated surfactant wastewater at current densities of 1.25 and 0.5 A $dm^{-2}$, respectively.

Fig. 4 shows that the $BOD_5$/COD ratio of the El-Fe pretreated wastewater increased from 0.27 to 0.58. Similar results were obtained by Wang et al. [13] who found that the wastewater pretreated by means of coagulation–flocculation with 600 mg $L^{-1}$ $Fe_2{}^{+}$, the value of $COD_B$/COD increased from 0.3 to 0.6 after 2 days acclimation period ($COD_B$ is the total COD which can be biodegraded).

Sludge formed by EC (Fe and Al) tends to be readily settable and easy to dehydrate. In fact, flocs formed by EC are similar to chemical floc, except that EC floc tends to be much larger, contains

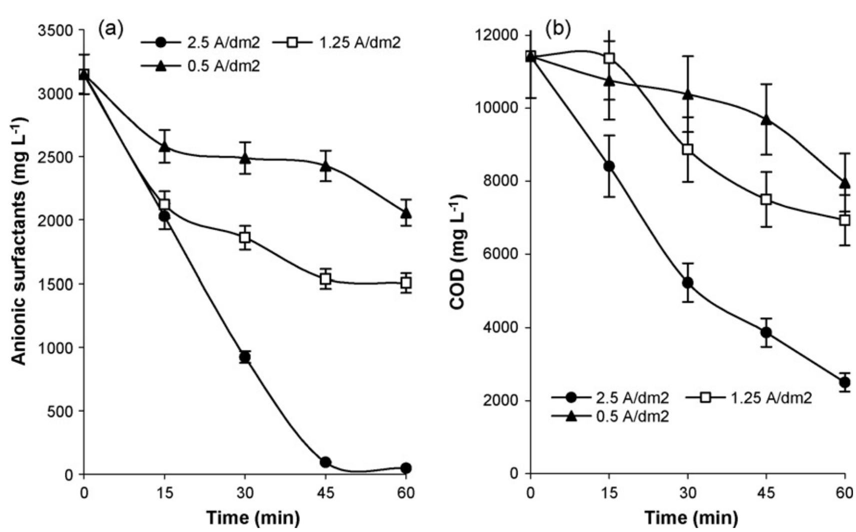


**Fig. 2.** The evolution of (a) anionic surfactants concentrations and (b) COD during the electro-flocculation of the industrial wastewater using Fe electrodes at different current densities. (●) 2.5 A $dm^{-2}$, (□) 1.25 A $dm^{-2}$, and (▲) 0.5 A $dm^{-2}$. Data points are the average of three replicates, and the error bars shown are the standard deviation.

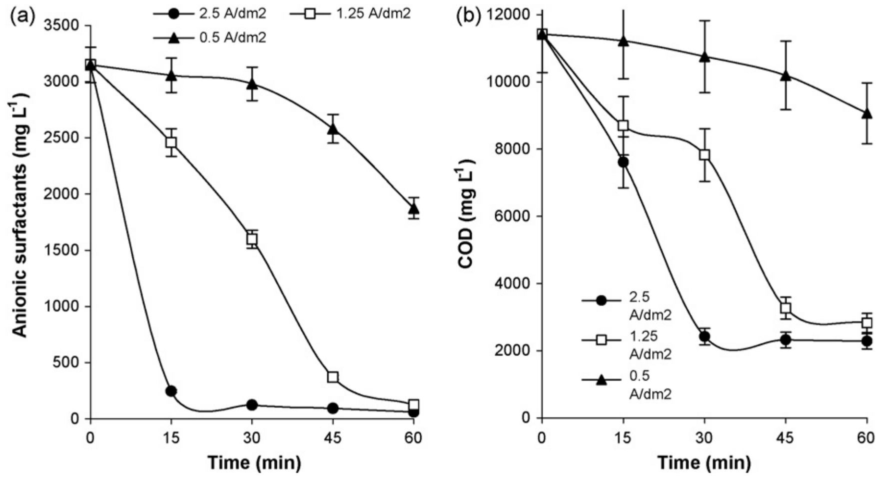


**Fig. 3.** The evolution of (a) anionic surfactants concentrations and (b) COD during the electro-Fenton pretreatment of the industrial wastewater at a $H_2O_2$ concentration of 1 mL $L^{-1}$ and at different current densities. (●) 2.5 A $dm^{-2}$, (□) 1.25 A $dm^{-2}$, and (▲) 0.5 A $dm^{-2}$. Data points are the average of three replicates, and the error bars shown are the standard deviation.

less bound water, is acid-resistant and more stable, and therefore, can be separated faster by filtration [14].

### 3.4. Pretreatment of the surfactant wastewater by electro-Fenton process (EL-Fenton)

The Fenton oxidation process has also been employed successfully to treat different industrial wastewaters in many previous investigations [15–17].

The formation of the hydroxyl radicals is at the base of the process of EL-Fenton. This reaction constitutes a process of advanced oxidation appropriate to the water treatment contaminated by organic pollutants [18]. EL-Fenton oxidation process was studied successfully for the treatment of olive mill wastewaters [19].

The purpose of this study is to conduct experimental tests employing the EL-Fenton oxidation process in treating the surfactant wastewater. The optimal pH for $Fe^{2+}/H_2O_2$ oxidation of the organic compounds is around 4 [20]. The reduction in the efficiency of the EL-Fenton reaction for values of pH higher than 4 is generally due to the iron precipitation. It can be also owing to a decomposition of hydrogen peroxide [21], oxidation of $Fe^{2+}$ by an oxidant other than ($H_2O_2$) [20], or a reaction between ($Fe^{2+}$) and ($H_2O_2$) not producing hydroxyl radicals [20].

The reagents implemented during the Fenton reaction are $Fe_2{}^+$ and $H_2O_2$. During Fenton reaction there is an oxidation of the ion ($Fe_2{}^+$) leading to the formation of the radical ($HO^\bullet$). Results showed that it is possible to use the EL-Fenton process to degrade anionic surfactants in the industrial wastewater in a short time (Fig. 3). This is on line with Wang et al. [13] showing that Fenton oxidation was a feasible treatment for wastewater containing a large amount of surfactants.

During the EL-Fenton oxidation process, a large amount of flocs of various sizes in the wastewater were observed. The small flocs were probably ferric hydroxo complexes formed by complex chain reactions of ferrous and hydroxide ions [22]. Those small flocs were not easy to settle out in wastewater because of their small sizes. The necessary time sufficient to the decantation of the treated wastewater is about 4 h.

The objective of the physicochemical pretreatment of the industrial wastewater is to improve its biodegradability. Therefore, $BOD_5$ was analysed before and after treatment by different processes. The use of $BOD_5$/COD ratio as indicator of biodegradability is advantageous over the single $BOD_5$ since this parameter gives information on the extent of total oxidation that had occurred during different treatments. Fig. 4 shows that EL-Fe and EL-Fenton processes improved the biodegradation of the industrial effluent. In fact, the ratio $BOD_5$/COD reached 0.79 in the case of EL-Fenton process. Wang et al. [13] found that the application of 60 and 120 mg $L^{-1}$ $H_2O_2$ during the pretreatment of a surfactant wastewater by Fenton oxidation resulted in an increase in $COD_B$/COD from 0.3 to 0.9 and from 0.3 to 0.7, respectively. On the other hand, the pretreatment of the industrial effluent by lime-alum and El-Al processes caused the decrease in the ratio $BOD_5$/COD. Tests of biological treatment of raw industrial effluent and pretreated were carried out to confirm the results of the $BOD_5$ analysis.

### 3.5. Biological treatment of the industrial wastewater

Experiments of biological treatment of the industrial wastewater pretreated by different processes were undertaken in order to select the adequate pretreatment process. *C. braakii*, as an isolate bacterium able to degrade a wide spectrum of anionic surfactants with interesting kinetics [5] was used in this study. This strain can be reproducibly used in separate biodegradation assays. The pH, concentrations of chemical oxygen demand and anionic surfactants were followed throughout the biodegradation experiments.

The pH showed an acidification during the treatment of the pretreated effluent by EL-AL and lime-alum. For EL-Fe and EL-Fenton

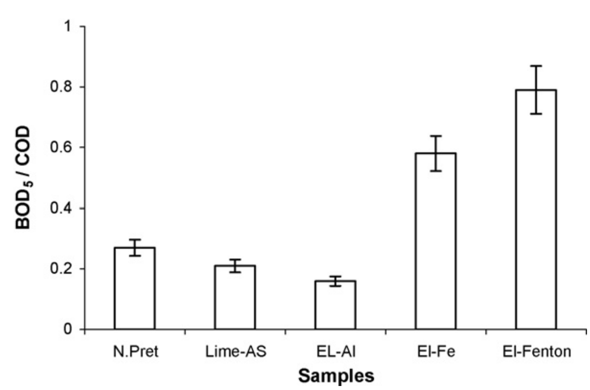


**Fig. 4.** The effect of different physicochemical pretreatment processes on the report $BOD_5$/COD of the pretreated industrial wastewater. Data points are the average of three replicates, and the error bars shown are the standard deviation.

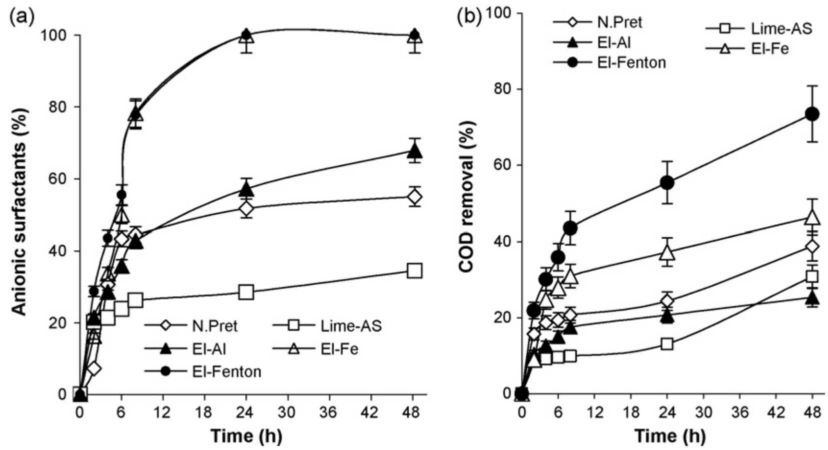


**Fig. 5.** The evolution of (a) anionic surfactants and (b) COD during biological treatment of the industrial wastewater not pretreated (◊), and lime-AS (□), El-Al (▲), El-Fe (△) El-Fenton (●) pretreated. Data points are the average of three replicates, and the error bars shown are the standard deviation.

pretreated effluent, an increased pH reaching values around 8 was observed (data not shown).

Concerning anionic surfactants and COD removals, high yields were obtained with the EL-Fenton pretreated effluent reaching 100 and 73% of anionic surfactants and COD removals, respectively after 48 h of culture (Fig. 5). This is on-line with Kitis et al. [23] finding who reported that Fenton's oxidation pretreatment was successful at increasing both the extent and rate of biodegradation of the studied surfactant compounds. Also, Wang et al. [13] found that a small amount of $H_2O_2$ can significantly increase both the rate and the extent of biodegradation of wastewater.

The treatment of raw industrial wastewater shows that anionic surfactants and COD removals are higher than those obtained with EL-Al and lime-alum. The low biodegradation of the lime-alum and El-Al pretreated effluents can be explained by the accumulation of the aluminium ions which inhibit the bacterial growth. Moreover, Liwarska-Bizukojc et al. [24] reported that the presence of high concentration of synthetic surfactants in wastewaters decreased the affinity of biomass to substrate.

The biological treatment of EL-AL pretreated effluent showed a decrease of 60 and 20% of anionic surfactants and COD, respectively, after 48 h of culture (Fig. 5). However, the biological treatment of lime-alum pretreated effluent resulted in low anionic surfactants (30%) and COD (20%) removals.

Table 1 shows the increase of iron concentration in the (EL-Fe and EL-Fenton)-biological treated wastewater. In fact, during the electrolysis treatment of wastewater, a certain amount of iron was continuously dissolved into the effluent from the cast iron anodes, as governed by the Faraday's law [25].

Results obtained after biological treatment of the EL-Fenton and El-Fe pretreated effluents (Table 1) show that the physicochemical characteristics of the final effluent respect the Tunisian discharge standards (COD < 1000 mg $L^{-1}$, $BOD_5$ < 400 mg $L^{-1}$, 6.5 < pH < 9, TSS < 400 mg $L^{-1}$, total nitrogen < 100 mg $L^{-1}$).

## 4. Conclusion

The presence of surfactants at high concentration in biologic stations causes an inhibition of autochthons microorganisms and produce foams which causes the perturbation of treatment process.

The treatment of wastewaters rich in anionic surfactants by bioaugmentation with bacteria with high catabolic capacities for the degradation of these substrates could be a suitable solution for the treatment of the industrial effluents generated by cosmetic and detergent factories. *C. braakii* is a powerful strain having a wide anionic surfactant degradation spectrum and possessed higher degradation kinetics than conventional biological systems. For example, the elimination rate of sodium lauryl ethyl sulphate by *C. braakii* was 0.15 g $L^{-1}$ $h^{-1}$ [5]. High anionic surfactant feed into the reactor could play a selective pressure for maintaining high *C. braakii* proportion [5,26]. This can justify the possibility to apply *C. braakii* in industrial wastewater treatment. Real experiments performed in two different industrial plants confirmed the necessity of starting the system with *C. braakii* in order to remove completely the foam and to reach the steady state (consistent biomass in the reactor, almost surfactant concentration below 10 ppm). After this start-up, a powerful biomass consortium is formed step by step. However, *C. braakii* is not efficient in degrading very high concentration (ex: 3000 mg $L^{-1}$) of sodium lauryl ethyl sulphate and non-ionic surfactants. An adequate physicochemical pretreatment is deemed necessary to decrease the surfactant load facilitating the biodegradation process.

The biological treatment of the industrial effluent, as well as the pretreated effluents by the different physicochemical processes showed that the best yields were obtained with the effluent pretreated by electro-Fenton process. The results show that EL-Fenton oxidation was a practical treatment for industrial wastewaters containing high amount of surfactants and organic compounds, allowing significant surfactants removals. Also, EL-Fenton oxidation was highly effective at enhancing the biodegradability of surfactant wastewater.

Wastewater containing a large amount of surfactants and COD cannot be easily treated either by conventional physicochemical nor biological processes, or even by selective strain. Combining Fenton oxidation and aerobic biological or EL-Fe oxidation and aerobic biological processes would provide the most sustainable way to solve this problem. This integration of electro-Fenton process prior to biological (aerobic or anaerobic) process already demonstrated its efficiency with olive mill wastewater treatment [19] and can be generalized to other industrial wastewaters such as textile, tannery, and petroleum effluents.

## Acknowledgment

Authors thank Agence Universitaire Francophone (AUF) for their financial support of the PER-LBP project.

## References


[1] ADEME: Agence de l'Environnement et de la Maîtrise de l'Energie, Direction de l'Agriculture et des Bioénergies. Tensioactif et Oléagineux Etude sur les matières premières oléagineuses disponibles sur le marché européen pour la production de tensioactifs, 2001.

[2] R.B. Cain, Biodegradation of detergents, Current Opinion in Biotechnology 5 (3) (1994) 266–274.

[3] G.F. White, N.J. Russel, Biodegradation of anionic surfactants and related molecules, Biochemistry of Microbial Degradation (1993) 143–177.

[4] S. Sayadi, A. Dhouib, N. Hamad, Tunisian Patent No. 17379, Procédé de traitement des tensioactifs et de microorganismes appropriés à ce procédé, 2001.

[5] A. Dhouib, N. Hamad, I. Hassairi, S. Sayadi, Degradation of anionic surfactants by *Citrobacter braakii*, Process Biochemistry 38 (2003) 1245–1250.

[6] Tunisian Norms, Agents de surface-Détergents, Agents de surface anioniques, Détermination de la biodégradabilité, NT 01-28, 1983.

[7] R.J. Knechtel, A more economical method for the determination of chemical oxygen demand, Water Pollution Control (May/June 1978) 25–29.

[8] American Public Health Association/American Water Works Association/Water Environment Federation, Standard Methods for the Examination of Water and Wastewater, American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA, 1992.

[9] J. Kjeldahl, A new method for the determination of nitrogen in organic matter, Zeitschrift Analytical Chemistry 22 (1883) 366.

[10] A.I. Zouboulis, A. Avranas, Treatment of oil-in-water emulsions by coagulation and dissolved-air flotation, Colloids and Surfaces A: Physicochemical and Engineering Aspects 172 (2000) 153–161.

[11] A.L. Ahmad, S. Sumathi, B.H. Hameed, Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC, Chemical Engineering Journal 118 (1/2) (2006) 99–105.

[12] P. Cañizares, B. Louhichi, A. Gadri, B. Nasr, R. Paza, M.A. Rodrigo, C. Saez, Electrochemical treatment of the pollutants generated in an ink-manufacturing process, Journal of Hazardous Materials 146 (2007) 552–557.

[13] X.-J. Wang, Y. Song, J.S. Mai, Combined Fenton oxidation and aerobic biological processes for treating a surfactant wastewater containing abundant sulfate, Journal of Hazardous Materials (2008), doi:10.1016/j.jhazmat.2008.02.117.

[14] M. Yousuf, A. Mollah1, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC)—science and applications, Journal of Hazardous Materials B 84 (2001) 29–41.

[15] M. Barbeni, C. Minero, L. Pellizzetti, Chemical degradation of chlorophenols with Fenton's reagent, Chemosphere 16 (1987) 2225–2232.

[16] K.W. Kuo, Decolorizing dye wastewater with Fenton's reagent, Water Research 26 (1992) 881–889.

[17] S.H. Lin, M.L. Chen, Purification of textile wastewater effluents by combined Fenton process and ion exchange, Desalination 109 (1997) 121–131.

[18] H. Zhang, D. Zhang, J. Zhou, Removal of COD from landfill leachate by electro-Fenton method, Journal of Hazardous Materials 125 (2005) 166–174.

[19] S. Khoufi, F. Aloui, S. Sayadi, Treatment of olive mill wastewater by combined process electro-Fenton reaction and anaerobic digestion, Water Research 40 (10) (2006) 2007–2016.

[20] H. Gallard, J. De Laat, B. Legube, Effect of pH on the oxidation rate of organic compounds by FeII/$H_2O$. Mechanisms and simulation, New Journal of Chemistry (1998) 263–268.

[21] J. Kiwi, C. Pulgarin, P. Peringer, M. Gratzel, Benifical effect of homogeneous photo-Fenton pretreatment upon the biodegradation of anthraquinone sulfonate in wastewater treatment., Applied Catalysis B: Environmental 3 (1993) 85.

[22] H.L. Sheng, M.L. Chi, G.L. Horng, Operating characteristics and kinetic studies of surfactant wastewater treatment by Fenton oxidation, Water Research 33 (7) (1999) 1735–1741.

[23] M. Kitis, C.D. Adams, G.T. Daigger, The effects of Fenton's reagent pre-treatment on the biodegradability of non-ionic surfactants, Water Research 33 (11) (1999) 2561–2568.

[24] E. Liwarska-Bizukojc, R. Scheumann, A. Drews, U. Bracklow, M. Kraume, Effect of anionic and nonionic surfactants on the kinetics of the aerobic heterotrophic biodegradation of organic matter in industrial wastewater, Water Research 42 (2008) 923–930.

[25] D. Pletcher, F.C. Walsh, Industrial Electrochemistry, 2nd ed., Chapman and Hall, London, UK, 1990.

[26] A. Dhouib, N. Hdiji, I. Hassairi, S. Sayadi, Large scale application of membrane bioreactor technology for the treatment and reuse of an anionic surfactant wastewater, Process Biochemistry 40 (8) (2005) 2715–2720.