Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.26930

220 (2021) 265–276
April

The feasibility of combining an electrocoagulation process and a biological treatment for the degradation of cutting oil emulsions

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Received 22 June 2020; Accepted 16 December 2020

ABSTRACT

This present study considered the evaluation of the feasibility of combining an electrocoagulation (EC) process with a biological treatment for cutting oil emulsions (COE) biodegradation. The optimization of the EC process by means of the second-order model obtained using a central composite design methodology led to the following optimal conditions: an initial pH of 5.8, a current density of 241 A m^{-2} and an electrolysis time of 29 min. Under these optimal conditions, chemical oxygen demand (COD), and turbidity reductions were, respectively, 97.42% and 99.97%. Despite the significant reduction in pollution, the final COD values remained always high. Therefore, the effluents pretreated by electrocoagulation were then treated in an aerobic bioreactor coupled to a sequential respirometer for 52 d. The obtained results were very satisfactory showing an additional COD reduction of more than 98.5%, accompanied by a good biomass activity (40 mg O_2 L^{-1} h^{-1}) for the pretreated COE. Moreover, the non-pretreated COE solutions reached COD reduction of 94% during 33 d of running after 52 d of the biomass acclimatization period. A total COD removal of 99.8% was obtained with a residual value of 177 mg L^{-1}, indicating the success of a biological treatment combined to an electrocoagulation pretreatment process.

Keywords: Biological treatment; Electrocoagulation; Cutting oil emulsion; Central composite design; Respirometry; COD

1. Introduction

The metalworking industries use large quantity of cutting oil emulsions (COE) in a variety of machining for lubrication, cooling, corrosion prevention, cleaning, and improving the work piece surface quality.

COE is a complex mixture of many compounds including water (refrigerant), mineral, vegetable, synthetic and semi-synthetic oils, surfactants, corrosion inhibitors, biocides, and other additives of high pressure, anti-wear, antifoam, etc. [1]. These emulsions are very stable, due to the presence of surfactants and co-surfactants. After a certain period of use, COE lose their cooling properties and need to be replaced. They cannot be released directly for obvious reasons of toxicity which remain problematic for the environment and might have a negative impact on the aquatic life. Furthermore, problems arise during their biological treatment [2,3]. Therefore, it is necessary to treat the emulsion before its release into the environment.

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Various wastewater treatment technologies have been tested for the treatment of COE, focusing on both physicochemical and biological methods. The physicochemical techniques such as chemical destabilization [4,5], centrifugation [6], and membrane processes [7–9] have shown several technical benefits for this treatment, but expensive equipment and high reagent are required, hence limiting their use. On the other hand, biological methods such as activated sludge process and anaerobic treatment [10–12], which are low cost effective for wastewater treatment do not always appear as adequate for the treatment of COE, because of their low biodegradability. Therefore, it is necessary to consider a more efficient treatment process.

The EC process has proven to be highly effective, as confirmed by its several achieved performances in the treatment of various types of water and wastewater, even containing organic or inorganic pollutants [13–15]. This process can be regarded as an alternative to conventional coagulation with several advantages such as ease of use, low produced sludge quantities, simple equipment, short operating time, low operating costs, and no use of chemicals usage. Consequently, there is no need to neutralize excess chemicals and no secondary pollution problems [16,17]. The efficiency of the EC process depends on several factors such as electrical current density, solution pH, electrode materials, etc. [18].

Generally for the industrial wastewater treatment, using a single process does not appear as effective as using a combination of processes [19]. Currently, research is focusing on the combination of process development based on electrochemical technologies.

Indeed it is gaining an increasing interest as a promising alternative pretreatment prior to various treatment methods such as advanced oxidation processes [20–22], ultrafiltration processes [23,24], microfiltration [25,26], and biological treatment [27–29]. These combinations can be used to remove a wide range of pollutants and secure good quality effluent.

Gutiérrez et al. [30] achieved a good improvement in chemical oxygen demand (COD), reaching 70% when the combination of destabilization/settling, ultrafiltration, and vacuum evaporation processes was used in metalworking fluids treatment. Furthermore, Milić et al. [31] investigated the use of electrocoagulation (EC) pretreatment prior to microfiltration of COE and as a result, EC pretreatment improved permeability of the membrane and achieved the best treatment performance with oil removal reaching up to 70% for the highest concentrations of the used cutting-oils (1%).

Recently, the combination of the electrochemical process with biological treatment has gained a considerable interest due to its ability to produce more biodegradable materials and to reduce the biodegradation process time [32]. For example, Yahiaoui et al. [33] proposed a combination of an electrochemical pretreatment on Pb/PbO_2 electrode with biological treatment for the degradation of methylene blue dye and the results showed that the percentage removal of COD was close to 92.03%. Another study by Yahiaoui et al. [34] studied the performance of an electrochemical pretreatment on a carbon electrode and a biological treatment for the degradation of tetracycline and tylosin from aqueous solutions where an improvement of the BOD_5/COD ratio from 0.033 to 0.46 for tetracycline and from 0.04 to 0.33 for tylosin were achieved. Madi et al. [35], proposed a combination of the EC process and the biological treatment for basic red dye removal and the results showed a highly efficient process, with a biodegradability ratio (BOD_5/COD) improvement from 0.05 to 0.35. Therefore, the performance of an EC process can be improved significantly in combination with biological treatment.

Only a few studies have been carried out on the use of electrochemical reactor coupled with biological treatment of the cutting oil emulsion treatment. Therefore, the objective of the present experimental study is to explore the feasibility of a combined process of electrocoagulation and aerobic biological treatment for the purification of synthetic and used cutting oil emulsion.

First, a response surface method (RSM) based on the central composite design (CCD) was applied for modeling and optimization of COD and turbidity removals in a batch reactor under operating conditions (pH, current density, and electrolysis time). The electrocoagulation alone is not enough to reduce the values of turbidity and COD to standards, hence the need for another treatment.

Secondly, respirometric tests were performed to measure bacterial activity by determining the rate of oxygen consumption (OUR) through the biomass. Finally, the aerobic biodegradability of samples pretreated and non-pretreated were estimated.

2. Materials and methods

2.1. Analytical methods

COD was measured using the test Merck COD Spectroquant®, in the range of 25–1,500 mg L^{-1} and 500–10,000 mg L^{-1} and a spectrophotometer NOVA 60 (Merck, Germany). Turbidity measurements were carried out using a turbidimeter of the type HACH model 2100N IS® (HACH Company, USA). Volatile suspended solids (VSS) content were determined by drying the samples at 105°C until constant weight, afterwards these samples were burned in a muffle furnace (controller B170-Naberthern, Germany) at 550°C, for 2 h, cooled in a desiccator and weighted.

2.2. Organisms and materials

The wastewater used in this study consisted of an aqueous emulsion solution of 4% v/v prepared from concentrated cutting oil (Tasfalout22B, Naftal, Algeria), denominated synthetic cutting oil emulsion (SCOE). Moreover, used cutting oil emulsion samples was supplied by mechanical parts manufacturing factory ETRAG (Agricultural Tractor manufacturing company, Constantine Algeria) and it was denominated spent cutting oil emulsion (SpentCOE). The collected SpentCOE samples were stored at 4°C.

Prior to EC experiments, sodium chloride (NaCl) solution at a concentration of 1.5 g L^{-1} was added to cutting oil samples to increase its electrical conduction [36]. The properties of SCOE and SpentCOE samples used in this study are given in Table 1. It can be noticed that the pollution values was very high in terms of COD and turbidity. However, the SCOE turbidity was almost half of the SpentCOE due to the presence of metallic particles transferred during the process.

Table 1
Properties of the SCOE and SpentCOE

Parameters	SCOE	SpentCOE
pH	8.78	6.55
Conductivity (µS cm^{-1})	160	2,020
Color	White	White
COD (mg L^{-1})	89,900	82,000
Turbidity (NTU)	38,000	68,880

Furthermore, activated sludge, used in the biological treatment assessment, was obtained from the municipal wastewater treatment plant at Pontivy, France.

2.3. Electrochemical treatment

Electrocoagulation experiments were carried out in a 0.6 L volume glass batch reactor. Cathode and anode were made of aluminum plates with an active area, for each electrode, of 52.8 cm^2. The electrodes were placed vertically parallel to each other with 15 mm spacing and connected to a DC power supply [MICROLAB powersupply, 0–80 V, 0–30 A] to insure a regulated current to the electrodes. A moderate magnetic stirring of 500 rpm, resulting from preliminary tests, was applied to the emulsion solutions in all tests. The initial pH of the solutions was adjusted by adding either NaOH (1 M) or H_2SO_4 (1 M). The different electrocoagulated samples were settled for 24 h prior to analyzing the supernatant. All experiments were carried out at room temperature.

2.4. Central composite design

In this study, the CCD was used to find cutting oil emulsion EC treatment optimal conditions. Three independent variables, initial pH (x_1), current density (x_2), and electrolysis time (x_3), were considered to influence the EC process. Whereas turbidity (Y_1), and COD reduction (Y_2) were considered as dependent variables. Each independent variable was coded at five levels: –1.68, –1, 0, +1, +1.68 (Table 2).

The original factors (x_1,x_2,x_3) are coded using the following equation:

$$X_i = \frac{x_i - x_{\text{cp}}}{\Delta x_i} \tag{1}$$

where X_i is the coded level, x_{cp} is the original value of the centered point and Δx_i is the step change value.

A total number of 18 experiments were required in this work, including 8 full factorial experiments, 6 axial experiments, and 4 repetitions of the central point. All statistical analyses were performed using MINITAB software (version 16).

A second-order polynomial equation was used to fit the experimental data and the general form of mathematical quadratic response equation is as follows [37]:

$$Y_i = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k-1}\sum_{j=2}^{k} b_{ij} x_i x_j + \sum_{i=1}^{k} b_{ii} x_i^2 + e \tag{2}$$

Table 2
Factors and coded levels of experimental design

Variable (x)	Factor range and levels				
	–1.68	–1	0	+1	+1.68
Initial pH (x_1)	5	5.75	6.5	7.25	8
Current density (A m^{-2}) (x_2)	100	150	200	250	300
Electrolysis time (min) (x_3)	20	27.5	35	42.5	50

where Y_i is the predicted response representing COD (Y_1) or turbidity (Y_2) reductions, b_0 is the regression coefficients for linear effects, b_i, b_{ij}, and b_{ii} the regression coefficients for quadratic effects, x_i and x_j are the studied coded factors (x_1: initial pH, x_2: current density (A m^{-2}), and x_3: electrolysis time (min)), and e is the error.

2.5. Biological treatment studies

The biological treatment assessment was performed on the EC pretreated samples under optimal conditions as well as on non-pretreated EC diluted samples. The experiments were carried out in a setup consisting of 2.5 L continuous aerated bioreactor ((Bioflo 3000, New Brunswick Scientific, USA) coupled to a sequential respirometer (INSA Toulouse, LISPB) [38].

Respirometric tests consist of monitoring in real time the respiratory activity of the sample (concentration of dissolved oxygen) by the biomass during degradation as an indicator of bacterial activity using a respirometer.

DO concentration may vary from saturation (~8 mg O_2 L^{-1}) to the minimum allowed concentration (~2 mg O_2 L^{-1}), before the possible appearance of bacterial stress.

Settled raw collected sludge samples of a biomass concentration of 5.6 g VSS L^{-1} were left overnight under continuous aeration in the bioreactor, prior to respirometric tests, so that all the remaining exogenous substrate was completely consumed and biomass reached endogenous state.

The sludge solution in the bioreactor was maintained at a temperature of 20°C, pH of 7.5, and mixed at 400 rpm. The samples in the respirometric cell were automatically replaced and recycled with aerated sludge from the bioreactor.

Oxygen concentration measurements were recorded by a computer and the rO_2 (OUR) was automatically calculated by slope measurement according to the following equation:

$$\frac{dC_{O_2}}{dt} = -rO_2 \tag{3}$$

Respirometric experiments were performed at varying COD concentrations in the bioreactor. The raw activated sludge was gradually acclimatized with the cutting oil emulsion in the bioreactor. When endogenous respiration was reached, a known mixed liquor volume was sampled, centrifuged at 8,500 rpm for 10 min and soluble COD and VSS were determined. In order to preserve biomass concentration in the bioreactor, the solids from the centrifuged samples were returned back.

The sampled volume was replaced back into the bioreactor with different volumes of EC pretreated solution (PSCOE) which were varied between 50 and 1,000 mL.

After 52 d biomass acclimatization period to PSCOE, this acclimatized biomass of a concentration of 1.06 g VSS L^{-1} was then used in the treatment of diluted SCOE in a soluble COD concentration of 3,125 mg O_2 L^{-1}. This experiment lasted 30 d with the same procedure as described (for PSCOE) for adding substrate. It should be mentioned that nutrients were added to the different oil emulsion samples used in this study, consisting of (per liter): 404 mg of K_2HPO_4, 220 mg of KH_2PO_4, 50 mg of NH_4CL, 10 mg of $MgSO_4·7H_2O$, 1.85 mg of $CaCl_2·4H_2O$, 1.5 mg of $MnCl_2·4H_2O$, and 0.3 mg of $FeCl_3·6H_2O$, to avoid nutrients depletion. Moreover, no other carbon source was added during the biological treatment and the oil emulsion solutions pH was maintained at 7.5 by adding automatically NaOH solution.

To assess the activity of autotrophic and heterotrophic biomasses, acetate (120 mg L^{-1}) and ammonium chloride (40 mg L^{-1}) were added to the bioreactor at different time intervals, at the beginning and during the cutting oil emulsion biodegradation assessment experiments. Furthermore, Mohlman index (MI) was used to assess any effect on the settling properties of activated sludge.

3. Results and discussion

3.1. Electrocoagulation

3.1.1. Experimental design analysis

The experimental and predicted results of turbidity and COD removal efficiencies of the 18 experiments are shown in Table 3 where the independent variables (initial pH, current density, and electrolysis time) are shown under their coded format. The predicted results are obtained through the application of the CCD method.

Based on the experimental results, an empirical relationship between the response and the independent variables was obtained and expressed by the following second-order polynomial equations for COD (Y_1) and turbidity (Y_2) removal efficiencies (Eqs. (4) and (5)).

$$Y_1 = 99.726 - 5.432X_1 + 23.49X_2 + 17.501X_3 + 5.282X_1X_2 - 1.399X_1X_3 - 16.886X_2X_3 - 2.352X_1^2 - 12.903X_2^2 - 9.915X_3^2 \quad (4)$$

$$Y_2 = 7.2019 - 4.1086X_1 + 15.7213X_2 + 12.6802X_3 + 3.2599X_1X_2 + 0.1926X_1X_3 - 12.5229X_2X_3 - 2.2125X_1^2 - 8.3692X_2^2 - 6.6997X_3^2 \quad (5)$$

The results presented in Table 3 indicate a good agreement between the experimental and the predicted values of COD and turbidity removal efficiencies (the predicted values were obtained from the model (Eqs. (4) and (5)). Moreover, the good fitting of Eqs. (4) and (5) to the experimental data as confirmed by the high correlation coefficients obtained (R^2 = 99.09% for COD and R^2 = 99.50 % for turbidity). Furthermore, the adjusted R^2 (R^2_{adj}) verified as well the goodness of the fitting and its suitability, since it corrects R^2-value for the sample size and the number of terms in the model by using the degree of freedom in its computation [39].

Moreover, the obtained F-test values indicate the validity of the obtained polynomial equations. If F-values of the studied system are greater than the critical F one (from

Table 3
CCD design matrix for three test variables in coded units along with the experimental and predicted responses

Run	pH (x_1)	I (x_2) (A m^{-2})	t (x_3) (min)	Experimental COD removal (%)	Experimental turbidity removal (%)	Predicted COD removal (%)	Predicted turbidity removal (%)
1	–1	–1	–1	47.77	26.73	46.55	25.99
2	1	–1	–1	33.92	11.18	31.43	7.35
3	–1	1	–1	97.33	99.97	96.52	96.17
4	1	1	–1	97.26	99.88	94.44	98.68
5	–1	–1	1	97.32	99.97	96.57	97.57
6	1	–1	1	84.98	73.13	82.22	73.33
7	–1	1	1	97.52	99.98	96.45	100.20
8	1	1	1	97.48	99.98	95.14	97.12
9	–1.68	0	0	97.29	99.95	97.85	102.21
10	1.68	0	0	79.56	81.10	84.03	83.94
11	0	–1.68	0	44.53	21.44	47.09	23.72
12	0	1.68	0	97.50	99.93	99.97	102.73
13	0	0	–1.68	54.28	38.30	56.92	42.24
14	0	0	1.68	97.18	99.97	99.57	101.11
15	0	0	0	97.37	99.92	97.20	99.72
16	0	0	0	97.40	99.95	97.20	99.72
17	0	0	0	97.49	99.97	97.20	99.72
18	0	0	0	97.40	99.94	97.20	99.72

Fisher–Snedecor table, F = 3.18 with 95% significance) the model is significant. The obtained F-values from the analysis of variance (ANOVA) are 96.43 for COD removal and 175.55 for turbidity removal, which are significantly higher than the critical F-value (Table 4).

3.1.2. Optimization of the operating variables

The quadratic model (Eqs. (4) and (5)) obtained by the CCD was used to find the values of the independent variables (initial pH, current density, and electrolysis time) which give the optimum responses (COD and turbidity removal).

The contour (2D) plots of the quadratic model (Figs. 1 and 2) were drawn using MINITAB software with one variable kept constant, while varying the two others within the experimental ranges.

Figs. 1a and 2a illustrate the effects of initial pH and electrolysis time on the COD and turbidity removal efficiencies and current density kept constant at 200 A m^{-2}. As can be seen in this figure, pH did not have much effect at low times however as time increased its effect became more important on COD and turbidity removal efficiency. As noted, the decrease in COD and turbidity removal efficiency was caused by a pH increase; it can be explained by the evolution of aluminum ionic species in solution. Indeed, the form and rate of dissolved aluminum species changed with the pH, passing through Al^{3+}, $Al(OH)^{2+}$, $Al(OH)^{2+}$, and $Al(OH)^{4-}$ when the pH increased, indicating, thus, a change in the ionic charge.

Maximum removal efficiencies of COD and turbidity were in the ranges of –1.68 to 0.5 for pH and 0 to +1.68 for time. The similar behavior between COD and turbidity was probably due to the form of cutting oil in water, which was in emulsion rather in a soluble form, hence an equivalence between the measurement of the COD and turbidity.

Figs. 1b and 2b show the effect of current density and electrolysis time on COD and turbidity removal at pH = 6.5. As can be seen in the figure, higher COD and turbidity removal efficiency were achieved when current density and electrolysis time increased as stipulated by Faraday's law. A high current intensity allows high material quantity dissolution and the current density determines the coagulant flux (coagulant dosage rate). Generally, in the chemical coagulation, COD and turbidity removal efficiencies increased with increasing aluminum doses [40]. The current density also determines the rate of hydrogen bubble generation at the cathode. Indeed, a decrease in the size of the bubbles is caused by the increase in the current density, which causes rapid flotation of the pollutants and sludge due to a higher upward flow [41].

On the other hand, Figs. 1c and 2c illustrate the COD and turbidity removal as a function of current density and initial pH for an electrolysis time of 35 min. The figure shows a relatively weak effect when the pH increased except for high current densities where it relatively improved.

To obtain the highest COD and turbidity removal efficiencies, the optimum operating parameters values were determined using Eqs. (4) and (5) within MINITAB16 software. The optimum values of the independent variables for COD and turbidity removal were 5.8, 241.36 A m^{-2}, and 29.19 min for initial pH, current density, and electrolysis time, respectively.

Using the obtained optimal values of the operating parameters, the reductions in COD and turbidity were 97.42% and 99.97%, respectively. On the other hand, a reduction of 94.35% of COD and 99.93% of turbidity was obtained for the SpentCOE treatment by applying these obtained optimal conditions. The predicted removal efficiencies for SCOE using Eqs. (4) and (5) were 98.42% for COD and 100% for turbidity.

After an experimental verification on both SCOE and SpentCOE oil emulsions, using optimum conditions, the maximum removal efficiencies of COD and turbidity results indicate a very good agreement with the predicted values. This implies that the strategy to optimize the EC cutting oil emulsion treatment to obtain the maximum removal efficiencies using RSM methodology in this study was successful.

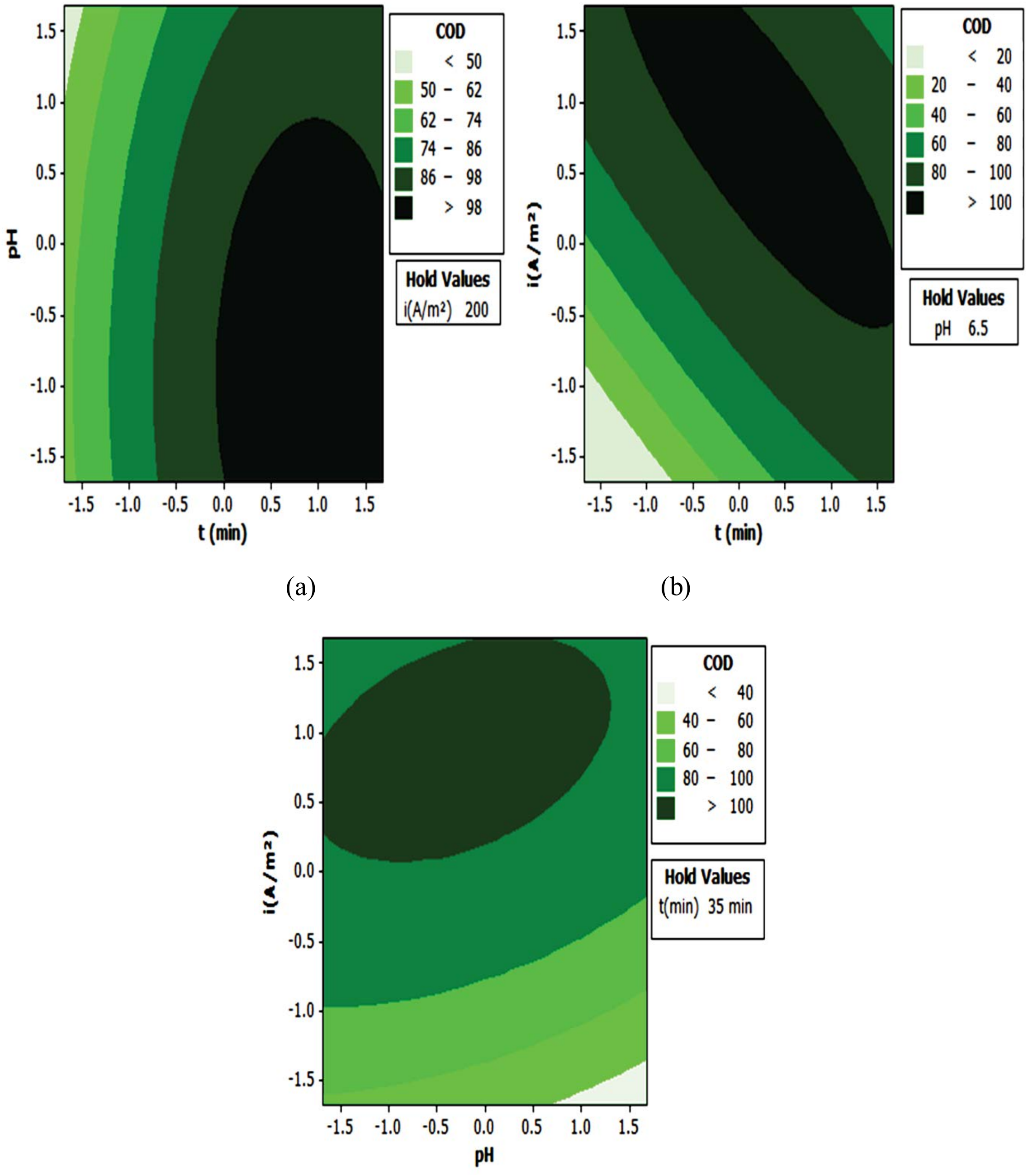
Although the COD EC reduction was very important, its value of 2,315 mg O_2 L^{-1} still remained important and higher than the Algerian national standards (executive decree N°. 06-141 of 19 April 2006, the aluminum and COD limit values are 3 mg L^{-1} and 300 mg O_2 L^{-1}, respectively), justifying the use of a biological treatment. Furthermore, the aluminum concentrations in the EC pretreated samples were 0.41 mg L^{-1} and <0.02 mg L^{-1} for SCOE and SpentCOE, respectively. These values are within the Algerian industrial liquid effluents discharge standards.

3.2. Biodegradability assessment

The structure of the remaining pollutants was altered through the use of electrochemical processes and became easily biodegradable and less toxic, allowing for further

Table 4
Analysis of variance (ANOVA) results for response parameters from central composite design

Responses	Source of variations	Sum of squares	Degree of freedom	Adjusted mean Square	F-value
COD	Regression	8,353.62	9	928.18	96.43
	Residuals	77.00	8	9.63	
	Total	8,430.62	17		
Turbidity	Regression	17,471.40	9	1,941.26	175.55
	Residuals	88.50	8	11.06	
	Total	17,559.80	17		



(a) (b)

(c)

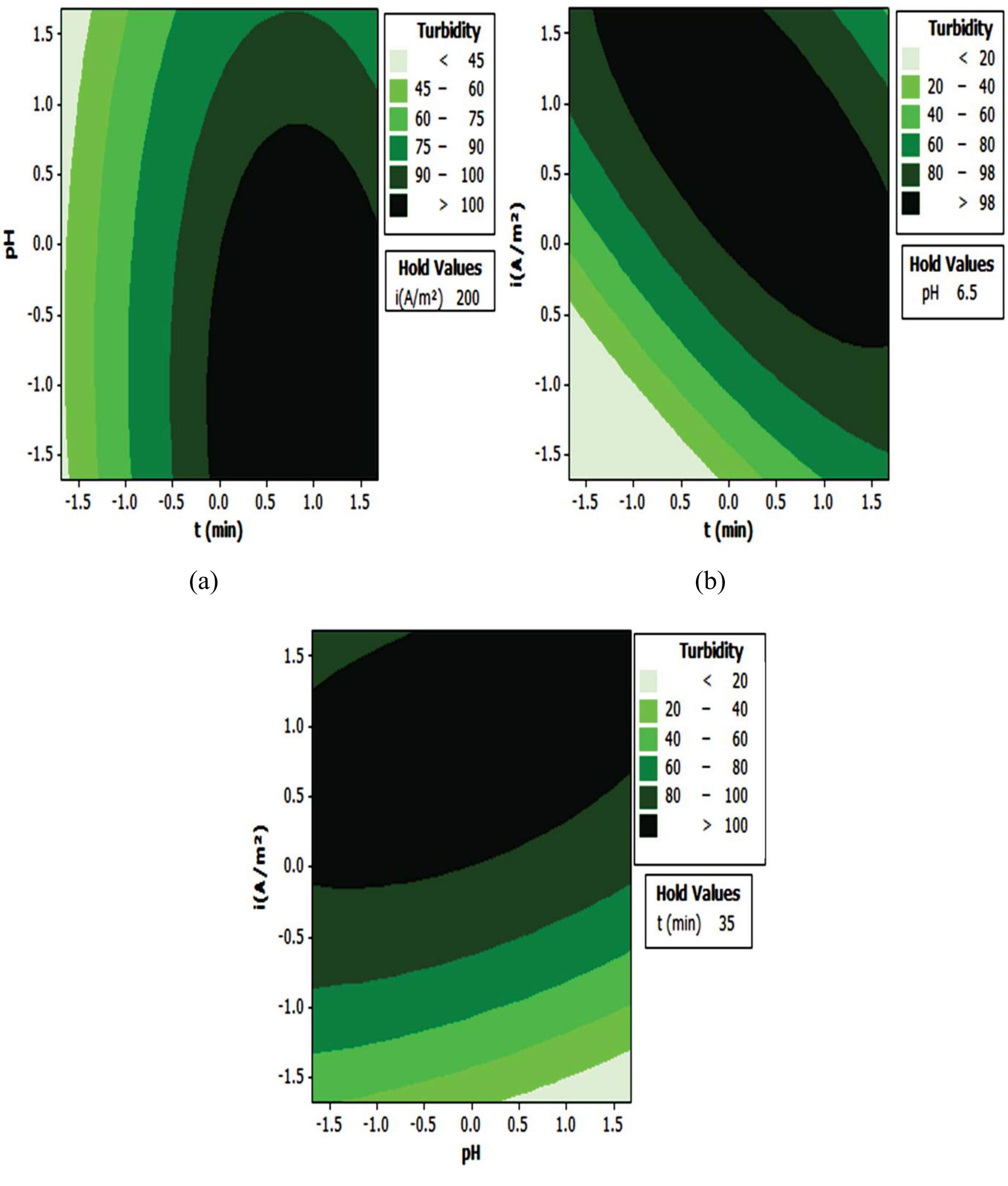
Fig. 1. Contour plots of COD removal efficiency as a function of: (a) initial pH and electrolysis time, (b) current density and electrolysis time, and (c) current density and initial pH in coded format.

biological treatment [33]. Even though biological methods did not always appear relevant for cutting oil emulsion removal, owing to their low biodegradability whereas coupling the biological treatment with physicochemical processes such as electrocoagulation could facilitate its biodegradation.

3.2.1. Biodegradation of acetate and ammonium chloride

Prior to the addition of COE to the bioreactor, sodium acetate, and ammonium chloride were added consecutively. The maximum exogenous oxygen uptake rates (OUR_{exomax}) obtained were 58.98 and 49.86 mg O_2 L^{-1} h^{-1} for acetate and ammonium chloride, respectively, for a consumption time period of 0.68 and 0.8 h, respectively. These experiments confirmed the good heterotrophic and autotrophic biomass activity.

However, the heterotrophic and autotrophic biomass activity decreased when electrocoagulation pretreated cutting oil emulsions (PSCOE) started to be injected consecutively to ammonium chloride and acetate as shown in



(a)

(b)

(c)

Fig. 2. Contour plots of turbidity removal efficiency as a function of: (a) initial pH and electrolysis time, (b) current density and electrolysis time, and (c) current density and initial pH in coded format.

Fig. 3. This also indicates a decrease of the heterotrophic activity from 58.98 to 18.5 mg O_2 L^{-1} h^{-1} to remain approximately constant hereafter. Whereas the autotrophic activity nearly ceased after 44 d of gradual decrease from 48.86 mg O_2 L^{-1} h^{-1} suggesting a total disappearance.

3.2.2. *Acclimatization of activated sludge*

Because of the specific characteristics of cutting oil emulsion, a biomass acclimatization was necessary through a gradual addition of COE to the bioreactor containing biomass while measuring COD removal efficiency and OUR.

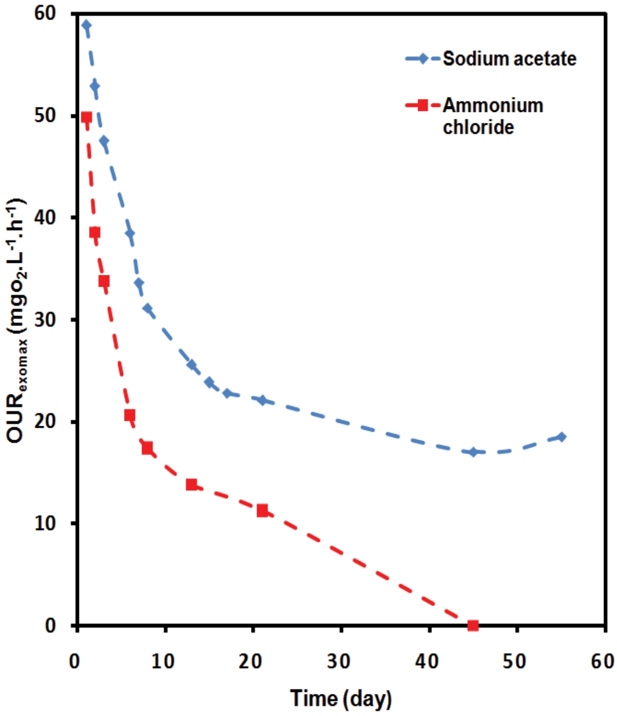


Fig. 3. OUR_{exomax} variation of sodium acetate ($C_2H_3NaO_2$) and ammonium chloride (NH_4Cl) during the acclimation period for PSCOE.

The experimental program considered first a PSCOE of about 2,315 mg L^{-1} of COD.

Fig. 4 shows a maximum for the exogenous oxygen uptake rate (OUR_{exomax}) variation and the cumulative COD removal efficiency for PSCOE and NPSCOE. The removal efficiency and the OUR_{exomax} were better for the PCOE. It can be seen from Fig. 4 that almost a month was required to reach an average cumulative COD removal efficiency of 98%. Moreover, the non-pretreated cutting oil emulsions (NPSCOE) (diluted SCOE) were found to be biodegradable as well, reaching an average cumulative COD removal efficiency of 94% during 33 d of running after 52 d acclimation using PSCOE. Then OUR_{exomax} remained almost constant (5 mg O_2 L^{-1} h^{-1}) during the first 18 d (Fig. 4a), a period corresponding most likely to an acclimatization of the biomass to the PSCOE. An increase was then observed, indicating an improvement in biomass activity reaching up 40 mg O_2 L^{-1} h^{-1}, considered as a convenient level [42].

Subsequently, the same biomass acclimatized by PSCOE was then used in the treatment of diluted SCOE (Fig. 5b), showing an increase in OUR_{exomax} from 1 to 7 mg O_2 L^{-1} h^{-1}. However, it was rather low for the NPSCOE with a maximum OUR_{exomax} of 7 mg O_2 L^{-1} h^{-1} comparatively to its high COD removal (94%). Indicating that the COD has been removed from the solution but not biodegraded so far, suggesting therefore a possible storage of the substrate according to ASM3 (activated sludge model 3) viewing the COD degradation pathway [43].

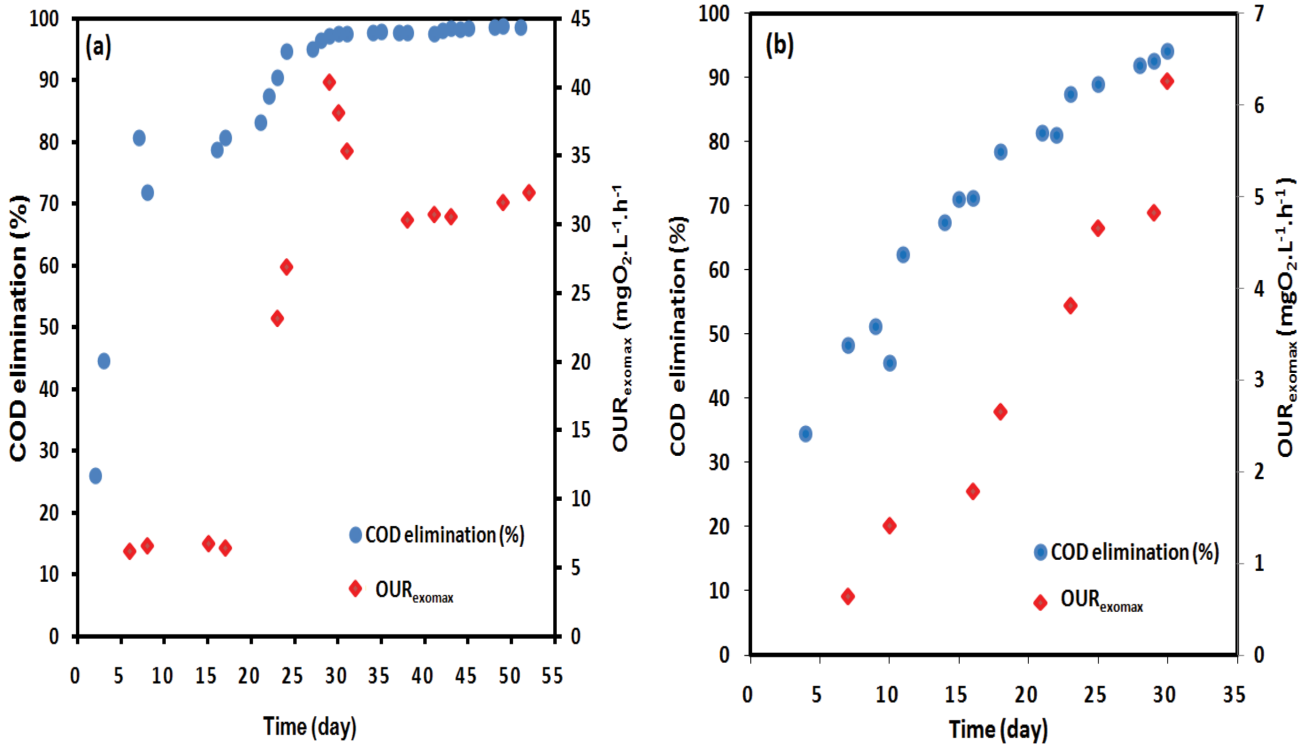


Fig. 4. Efficiency of COD elimination and OUR_{max} variation during the acclimation period for: (a) PSCOE and (b) NPSCOE ($T = 20°C$; pH = 7.5).

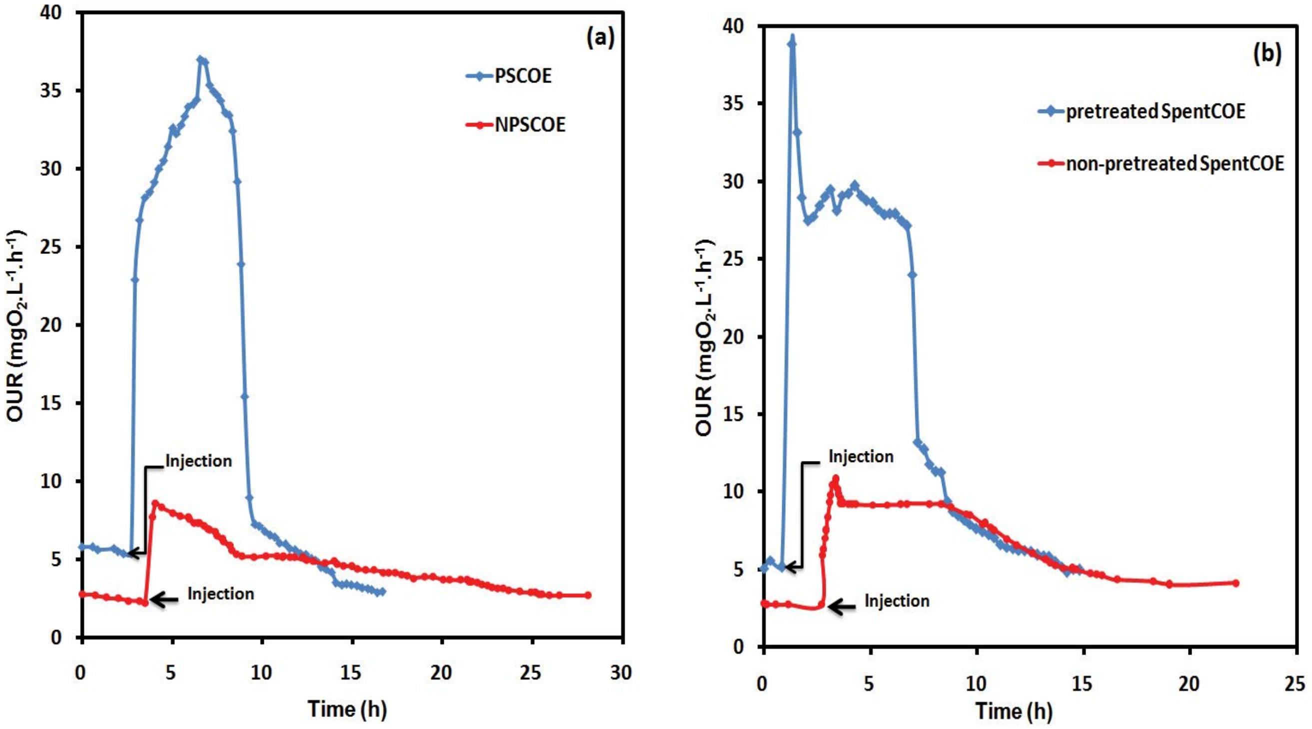


Fig. 5. Oxygen uptake rate (OUR) curves obtained for pretreated and non-pretreated: (a) SCOE and (b) SpentCOE ($T = 20°C$; pH = 7.5).

Therefore, from the obtained results, the combination of an electrocoagulation pretreatment with biological treatment showed that a total of 98.8% of initial COD was removed, confirming the relevance of the combined process.

From these experiments, the biomass growth yields ($Y_{X/S}$) for each response were determined and summarized in Table 5. They varied around average values of 0.57 and 0.89 for PSCOE and NPSCOE, respectively and their respective oxygen to substrate ratios ($Y_{O/S}$) are 0.43 and 0.11, meaning that the biodegradation of the NPSCOE consumed less energy. Moreover, the levels of COD removal efficiencies were quite similar and equal to 98% and 94%, respectively, for the two cutting oil samples, suggesting possible substrate storage for NPSCOE.

3.2.3. Evaluation of biodegradability

In order to estimate the biodegradability of pretreated and non-pretreated COE using activated sludge, respirometric tests were carried out via the following parameters, organic loading rate OLR = 0.45 kg DCO kg MVS^{-1} d^{-1}, hydraulic retention time HRT = 5 d and OLR = 0.41 kg DCO kg MVS^{-1} d^{-1}, HRT = 6.25 d, for PSCOE and NPSCOE, respectively. Moreover, tests on SpentCOE were carried out with (OLR = 0.67 kg DCO kg MVS^{-1} d^{-1}, HRT = 5.56 d) and (OLR = 0.29 kg DCO kg MVS^{-1} d^{-1}, HRT = 7.14 d) for pretreated and non-pretreated emulsions, respectively.

The resulting OUR profiles, for the PSCOE and NPCOE are represented in Figs. 5a and b, respectively which show that OUR for the PSCOE was high compared to NPCOE, hence, biodegradability of oil emulsion increased when EC pretreated emulsion was used.

The OUR profile showed, at the beginning of the experiment, a rapid increase, due to the degradation of the easily biodegradable COD, followed by a moderate one. For the PSCOE, 5 h were needed to reach the peak of 37 mg O_2 L^{-1} h^{-1} and for NPSCOE 1 h is needed to reach 8.7 mg O_2 L^{-1} h^{-1}. Moreover, it took about 1 h to reach a peak of 39 and 10.8 mg O_2 L^{-1} h^{-1} for SpentCOE pretreated and non-pretreated, respectively. It should be underlined that the form of the OUR curves of the pretreated and non-pretreated samples were similar in each considered case but the reached OUR_{max} were different. In addition, it is possible that the EC pretreated samples contained more biodegradable material than the non-pretreated ones because of the difference in biodegradation time periods and the OUR_{exomax} indicating that EC pretreatment improved oil emulsions biodegradation.

After the OUR increase, in Fig. 5a, a subsequent decrease was observed which was probably due to the hydrolysis of particulate COD or could be due to more difficult access to the remaining primary substrate (easily biodegradable) caused by substrate accumulation in sludge [44].

However, a rapid decrease of the SpentCOE OUR pretreated and non-pretreated was observed. This rapid decreases may be attributed to the depletion of the easily biodegradable substrate, after this step, the OUR fell to two consecutive levels, at about (28 and 12 mg O_2 L^{-1} h^{-1}) for the pretreated samples and at about (9.25 and 5 mg O_2 L^{-1} h^{-1}) for the non-pretreated one. Concerning the first part of the OUR curves down to the inflexion points the corresponding oxygen consumption was used for storage phase whereas oxygen consumption from the inflexion point down to endogenous respiration was used for biomass growth [45].

Table 5
Variation of the yields ($Y_{X/S}$, $Y_{O/S}$) during the acclimation period for (a) PSCOE and (b) NPSCOE

(a)

Time (d)	17	21	24	28	31	37	42	45	49	52
$Y_{X/S}$	0.62	0.66	0.63	0.55	0.53	0.38	0.44	0.65	0.57	0.60
$Y_{O/S}$	0.38	0.34	0.37	0.45	0.47	0.62	0.56	0.35	0.43	0.44

(b)

Time (d)	11	14	15	18	20	22	25	28	30
$Y_{X/S}$	0.95	0.91	0.98	0.78	0.92	0.86	0.85	0.96	0.94
$Y_{O/S}$	0.05	0.09	0.02	0.22	0.08	0.14	0.14	0.04	0.06

The obtained OUR curves due to samples injections in an aerated discontinuous reactor allowed the graphical identification and the calculation of the oxygen consumption used in the storage process. ASM3, supposed that all readily biodegradable substrate was stored as internal storage products and later would be used for growth during the famine phase [46]. Comparing storage and growth process in a discontinuous reactor, the storage process was faster and might be identified like a dominating mechanism, therefore, the storage yield value gave an idea on the storage magnitude.

According to Ordaz et al. [47], two growth yields can be defined, storage yield ($Y_{\text{XSto}/S}$) and storage growth yield ($Y_{X/\text{XSto}}$). Both yields can be estimated from the OUR curves using Eqs. (6) and (7) [45,47], where S_S is the injected substrate concentration.

$$Y_{\text{XSto}/S} = 1 - \left(\frac{\Delta O_{\text{XSto}/S}}{S_S} \right) \tag{6}$$

$$Y_{X/\text{XSto}} = \frac{Y_{X/S}}{Y_{\text{XSto}/S}} \tag{7}$$

The $Y_{X/S}$, $Y_{\text{XSto}/S}$, and $Y_{X/\text{XSto}}$ resulting for the SCOE and SpentCOE are summarized in Table 6. From Table 6, it can be seen that $Y_{\text{XSto}/S}$ is greater than $Y_{X/S}$ which suggested a storage phenomenon followed by growth. According to Henze [43], a low yield coefficient for storage ($Y_{\text{XSto}/S}$) and a higher one for subsequent growth ($Y_{X/S}$) allow to approximate the consequences of direct growth rather than storage followed by growth. The $Y_{\text{XSto}/S}$ values were affected by the electrocoagulation pretreatment, exhibiting decreases from 0.967 to 0.633 g COD g COD^{-1} for the SCOE and from 0.963 to 0.780 g COD g COD^{-1} for SpentCOE. These values explain the difference in oxygen consumption for the different considered cases and the obtained degradation.

Table 6
Summary of the estimated $Y_{X/S}$, $Y_{\text{XSto}/S}$, and $Y_{X/\text{XSto}}$ for the pretreated and non-pretreated SCOE and SpentSCOE

	Non-pretreated			pretreated		
	$Y_{X/S}$	$Y_{\text{XSto}/S}$	$Y_{X/\text{XSto}}$	$Y_{X/S}$	$Y_{\text{XSto}/S}$	$Y_{X/\text{XSto}}$
SCOE	0.94	0.967	0.971	0.57	0.633	0.899
SpentCOE	0.94	0.963	0.975	0.67	0.780	0.858

Apparently, the cutting oil emulsion is biodegradable even without pretreatment, with a COD reduction of up to 94% and 93% for NPSCOE and SpentCOE, respectively. However, a great difference in oxygen consumption resulted between the pretreated and the non-pretreated ones as shown in Table 7. Therefore, COD of the non-pretreated samples was mainly stored whereas for the pretreated ones COD was biodegraded.

Alinsafi et al. [48] proposed a biodegradability yield (Y_B) factor in comparing textile dyes biodegradability, using oxygen consumption and COD concentration injected as in Eq. (8):

$$Y_B = \frac{\left(\frac{V_{O_2}}{\text{COD}} \right) \text{pretreated}}{\left(\frac{V_{O_2}}{\text{COD}} \right) \text{non-pretreated}} \tag{8}$$

Consequently, according to Table 6, EC increased oil emulsions biodegradability for SCOE and SpentCOE by a factor of 8.23 and 3.61, respectively.

3.2.4. Effect of COE on the settling of activated sludge

The Mohlman index (MI) is mainly used for the characterization of biological sludge settling properties; it represents the volume occupied by 1 g of undiluted activated sludge. Activated sludge with good settling ability has an MI of 50–100 mL g^{-1} [49]. In this study, the MI results in the reactor were 77.03 and 76.92 for non-pretreated SCOE and SpentCOE, respectively, 80 and 75.54 for pretreated SCOE and SpentCOE, respectively. In the present study, the observed Mohlman index was between 50 and 100 mL g^{-1}. These values represent a normal value and a good settling ability. Therefore, there was no negative effect of cutting oil emulsion on the quality of activated sludge settling.

4. Conclusion

The use of CCD methodology allowed the determination of optimal conditions: initial pH of 5.8, electrolysis

Table 7
Biodegradability yields and the estimate parameters during respirometry tests

	Non-pretreated		Pretreated		
	$\mathrm{OUR}_{\mathrm{exomax}}$ (mg O_2 L^{-1} h^{-1})	V_{O_2} (mg L^{-1})	$\mathrm{OUR}_{\mathrm{exomax}}$ (mg O_2 L^{-1} h^{-1})	V_{O_2} (mg L^{-1})	Y_B
SCOE	6.27	25.8696	31.62	235.45	8.23
SpentCOE	5.41	15.7277	33.63	234.0013	3.61

time of 29.19 min, and current density of 241.36 A m^{-2} to achieve a COD and turbidity removal efficiency of 97.42% and 99.97%, respectively.

These obtained optimal parameters were applied to SpentCOE and led to satisfactory COD (94.35%) and turbidity (99.99%) removal efficiency.

The obtained results showed that the use of EC improved consequently COE biodegradability and bacterial activity. However, it should be mentioned that the high biological removal efficiency in the non-pretreated COE was attributed to substrate storage requiring more biological treatment time. Therefore, increasing biomass activity was surely an economical advantage when EC pretreatment was used resulting in additional removal efficiency of 98.5% through biological treatment with a residual COD of 177 mg L^{-1}. Moreover, the residual EC pretreated aluminum concentrations were less than 3 mg L^{-1}. These values were below the Algerian mechanical industry effluent liquids discharge standards (aluminum and COD limit values are 3 mg L^{-1} and 300 mg O_2 L^{-1}, respectively).

Finally, a total of 99.8% of the initial COD was removed when EC and aerobic treatment processes were combined. This clearly demonstrates the success of coupling the two processes in cutting oil emulsion treatment.

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