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Cutting Oil Emulsion Anaerobic Biodegradation: Electrocoagulation Pretreatment Effect

Aida Dermouchi*[a], Thomas Lendormi[b], Sihem Arris[a], Jean L. Lanoiselle[b], Mossaab Bencheikh-Lehocine[a]

[a]Université de Constantine 3, Laboratoire d'Ingénierie des Procédés de l'Environnement (LIPE), Faculté de Génie des Procédés. 25000 Constantine, Algérie.
[b]Université de Bretagne-Sud, FRE CNRS 3744, IRDL (Institut de Recherche Dupuy de Lôme), F-56300 Pontivy, France.
dermouchi_ad@hotmail.fr

In this study, the influence of electrocoagulation pretreatment, using aluminum electrodes, of spent and prepared cutting oil emulsions (Tasfalout22B,Naftal, Algeria), at 4 % v/v, biodegradation was examined under anaerobic conditions. Moreover, non-pretreated samples were tested as well.
The Automatic Methane Potential Test System (AMPTS) contained fifteen parallel reactors; each one was connected to a volumetric gas counter with an automatic acquisition system to follow gas production during biodegradation was used. Experiments were carried out in triplicate. 500 mL batch reactors were inoculated using anaerobic sludge from a municipal digester (Saint-Brieuc, France), at an inoculum to substrate ratio (I/S) of 3:1 and 2:1 w/w of volatile solids for non-pretreated and pretreated cutting oil samples respectively. These reactors were incubated in a thermostatically-controlled water bath at 37 °C. Electrocoagulation pretreatment optimum conditions were obtained using experimental design (18 experiments), for an initial pH of 5.8, current density of 241 A / m² and a processing time of 29 min. The anaerobic biodegradation tests were then carried out. The cumulative methane production increased, when pretreatment was used, from 0.024 ± 0.007 to 0.175 ± 0.05 (650 %) and 0.094 ± 0.04 to 0.27 ± 0.01 Nm^3 CH_4 kg COD^{-1} (187 %) for synthetic and spent cutting oil emulsion respectively. Furthermore, anaerobic biodegradability improved as well from 6.9 to 51 % and from 26.98 to 80 % for synthetic and spent cutting oil emulsion respectively. These results show the considerable improvements of cutting oil emulsion anaerobic biodegradation when electrocoagulation pretreatment was used.

1. Introduction

Anaerobic digestion (AD) is one of the oldest and successful technology applied for organic wastes stabilization (Lier et al., 2001). The use of AD for the treatment of organic products is considered to be a very suitable treatment due to its significant economic and environmental advantages such as, low energy consumption, low excess sludge production, enclosure of odors and aerosols (Edelmann et al., 2005).
This process is a natural biological one which consists of organic matter decomposition by a complex network of interacting and competing microorganisms under anaerobic conditions (absence of oxygen).
Digestion of organic matter generates both biogas (methane and carbon dioxide) and a solid residue (digestate) (Kheiredine et al., 2014). This process of organic matter valorization can therefore produce renewable energy and compost. The four steps of AD are hydrolysis, acidogenesis, acetogenesis and methanogenesis. The hydrolysis step is often the limiting step when organic matter is hard to degrade (Raposo et al., 2012). In this context, various pretreatment processes were investigated in order to improve biodegradation (Pilli et al., 2011). The effluents of the mechanical industries are mainly constituted of cutting oil emulsions which are considered poorly biodegradable and even toxic to the ecosystem.
Cutting oils emulsions (COE) are aqueous solutions generally occurring in a wide variety of industrial applications for lubrication and refrigeration during cutting and forming processes. These emulsions consist of mineral oils, water, surfactants, corrosion inhibitors and biocides mixtures (Krstić et al., 2007). Which could be considered hazardous to the environment, because of its long stay within it, since they are not readily

biodegradable and even toxic for ecosystems, so they have to be treated before releasing them into the environment. Due to their high chemical oxygen demand (COD),which varies in the range of 30 to 200 g $O_2.L^{-1}$ depending on the mineral oil percentage (Nakamura and Matsumoto, 2013).

Recently, electrocoagulation (EC) became one of the widely used pretreatment and post-treatment method for several wastewaters and raw water. In fact, Deshpande et al (2010) reported that the combined treatment system comprising EC and anaerobic fixed film fixed bed reactor is competitive and can be used effectively for high strength wastewaters. Therefore, EC process knows an increased popularity and a considerable technical improvements with a high potential to replace many complex treatment processes (Mollah et al., 2004). EC process based on the electrochemical dissolution of a sacrificial electrode and a generation of insoluble flocs of metal hydroxides, can be considered a process with a multitude of associated mechanisms contributing to the treatment of pollution in water. Its efficiency depends on the type of electrodes used.

The purpose of this study has been to test the effectiveness of EC process as a pretreatment method for treatment of spent and prepared cutting oil emulsions (Tasfalout22B,Naftal, Algeria), at 4 % v/v, under anaerobic conditions. Moreover, non-pretreated samples were tested as well. The electrocoagulation process was assessed using a response surface method (RSM) for the modeling and the optimization of COD and turbidity removal yields in a batch reactor using aluminum electrodes.

2. Materials and methods

2.1 Substrate and Inoculum

The wastewater used for this study consisted of an aqueous emulsion solution of 4% v/v (synthetic cutting oil emulsion) prepared from concentrated cutting oil (Tasfalout22B, Naftal, Algeria). Moreover, spent cutting oil emulsion samples, used in mechanical parts manufacturing factory, were collected from ETRAG (Agricultural tractor manufacturing company) located in Constantine, Algeria. Spent cutting oil emulsion samples were stored at 4°C in a fridge before further use. Sodium Chloride (NaCl) at a concentration of 1.5 g / L was added to cutting oil samples to increase electrical conduction for the EC pretreatment (Khemis et al., 2005).The characteristics of cutting oil emulsion samples are presented in table 1. Furthermore, batch reactors were inoculated using anaerobic sludge (Inoculum) from a municipal digester (Saint-Brieuc, France).

Table 1: Characterization of the synthetic and spent cutting oil emulsion

Parameters	synthetic	spent	inoculum
pH	8.78	6.55	8.11
Conductivity(µS/Cm)	160.00	2020.00	-
DCO (mg/L)	89900.00	82000.00	21000.00
Turbidity (NTU)	38000.00	68880.00	-
Volatile solids (g/L)	-	-	29.26

2.2 Analytical methods

In this study, COD was measured using the test Merck COD Spectroquant®, in the range of 500-10000 mgL^{-1} and a spectrophotometer NOVA 60 (Merck, Germany). The samples were poured into the COD tubes then closed tightly with screw cap before placing them into a thermo-reactor and heated for 2h at 150°C. The organic compounds are oxidized in a hot acidic medium. At the end COD is measured with a spectrophotometer. Turbidity measurements were carried out using a turbidimeter of the type HACH model 2100N IS®. VSS content were determined by drying the samples in a forced air circulation oven at 105 °C until constant weight, afterwards these samples were burned in a furnace at 550 °C, for 2h and cooled in a desiccator then weighted.

2.3 Electrocoagulation (EC) cell and procedure

In this study, cutting oil emulsion was first pretreated by electrocoagulation and then used as a substrate for the AD treatment. EC experiments were conducted in a batch reactor consisting of 0.6 L volume glass cell. Both electrodes (cathode and anode) were made of aluminum plates with an active surface area of 52.8 cm^2 for each electrode. The electrodes were placed vertically parallel to each other with a 15 mm spacing and connected to a DC power supply [MICROLAB Power supply, 0–80 V, 0–30 A], which was used in order to supply a regulated electrical current to the EC cell. 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 samples was adjusted by adding either NaOH (1M) or H_2SO_4 (1M). Electrocoagulated samples were allowed to settle for 24 hours and the supernatant was separated and used for analysis.

2.4 Experimental design

The effect of the initial pH (x_1), current density (x_2), and electrolysis time (x_3), on the EC treatment of the synthetic COE has been optimized by using a central composite design (CCD). Turbidity reduction (Y_1), and COD reduction (Y_2) are considered as dependent variables. The experimental plan was carried out as a full CCD consisting of 18 experiments, including 2^3=8 cube points, 4 replications at the center point of the design were used to allow an estimate of the sum of squares of pure error and 6 axial points (for more details see Table 3). The three quantitative dimensional variables (X_i) were coded as dimensionless terms (x_i) using Eq(1).

$$X_i = \frac{x_i - x_{cp}}{\Delta x_i} \quad (1)$$

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.
Table 2 Shows the range of the factors selected in this study (The ranges used in these studies are based on preliminary tests). The statistical software MINITAB (version 16) was used to fit the experimental data to the second-degree polynomial model with all possible interactions which related the responses (Y_1, Y_2) to factors (x_1, x_2, x_3), according to Eq (2) (Cho and Zoh, 2007):

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

Where (Y_i) is the predicted response representing COD reduction (Y_1) or turbidity (Y_2), 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 independent variables (i and j range from 1 to k), k is the number of independent parameters (k=3 in this study); and e is the error.

Table 2: Ranges and levels of experimental design

Variable (x)		Ranges and levels -2	-1	0	+1	+2
Initial pH	(x_1)	5	5.75	6.50	7.25	8
Current density (A/m²)	(x_2)	100	150.00	200.00	250.00	300
Electrolysis time (min)	(x_3)	20	27.50	35.00	42.50	50

2.5 Anaerobic digestion (AD)

In this study the biodegradability of a substrate during the anaerobic digestion was determined using an Automatic Methane Potential Test System (AMPTS, Bioprocess Control Sweden). AMPTS was an engineered analytical device developed for measurements of the methane production from the anaerobic digestion of biodegradable substrates. Among the advantages of this device, the real-time data logging of accumulated methane volume. This system was comprised of 15 incubation bottles, each one was connected to a volumetric gas counter with an automatic acquisition system.
To estimate the effect of EC on biodegradability, total methane production before and after substrate EC pretreatment was measured. The inoculum to substrate ratio (I/S) for biodegradability tests was set equal to 3:1 and 2:1 (w/w) for non-pretreated and pretreated cutting oil samples (synthetic and spent) respectively. The incubation bottles (500 mL) were inoculated using anaerobic sludge (inoculum) and substrate. Bottles were incubated under the anaerobic conditions in a thermostatically-controlled water bath at 37 °C. All the incubations were performed in triplicates.

3. Results and discussions

3.1 EC treatment studies

Based on the experimental results collected in Table 3, an empirical relationship between the response and the independent variables was obtained and expressed by the second order polynomial equations Eq(3) and Eq(4):

$$Y_1 = 97.2019 - 4.1086\, X_1 + 15.7213 X_2 + 12.6802\, X_3 + 3.2599 X_1 X_2 - 12.5229\, X_2 X_3 - 2.2125 X_1^2 - 8.3692\, X_2^2 - 6.6997 X_3^2 \quad (3)$$

$$Y_2 = 99.726 - 5.432 X_1 + 23.49\, X_2 + 17.501\, X_3 + 5.282\, X_1 X_2 - 16.886\, X_2 X_3 - 2.352\, X_1^2 - 12.903\, X_2^2 - 9.915 X_3^2 \quad (4)$$

Where (Y_1) and (Y_2) are COD and turbidity respectively;
In these equations, the insignificant terms were eliminated since they do not meet the statistical criteria.

Table 3: CCD design matrix showing codded values, experimental results and predicted.

				Experimental		Predicted	
Run	pH	i (A/m²)	t (min)	COD (%)	Turbidity (%)	COD (%)	Turbidity (%)
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	- 2	0	0	97.29	99.95	97.85	102.21
10	+2	0	0	79.56	81.10	84.03	83.94
11	0	- 2	0	44.52	21.44	47.09	23.72
12	0	+2	0	97.50	99.93	99.97	102.73
13	0	0	- 2	54.28	38.30	56.92	42.24
14	0	0	+2	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

The good fitting of equations (3) and (4) to the experimental data was verified through the high obtained correlation coefficients (R^2=99.09 % for COD and R^2=99.50 % for turbidity). Furthermore, the obtained adjusted R^2 (R^2_{Adj}) verified as well the goodness of the fitting and it is more suitable (consider the sample size and the number of terms in the model), the adjusted R^2 values (R^2_{Adj}= 98.06 % for COD and R^2_{Adj}=98.93 % for turbidity) are close to the R^2 ones. Moreover, the obtained F-values from the ANOVA (Analysis of variance) (Table 4) are, 96.43 for COD and 175.55 for turbidity, which are significantly higher than the critical F value (F=3.18 with 95% significance).

Table 4: Analysis of variance (ANOVA)

Responses	Source of variations	Sum of squares	Degree of freedom	Adjusted mean Square	F-value
(1)COD	Regression	8353.62	9	928.18	96.43
	Residuals	77.00	8	9.63	
	Total	8430.62	17		
(2)Turbidity	Regression	17471.40	9	1941.26	175.55
	Residuals	88.50	8	11.06	
	Total	17559.80	17		

In this study, the main objective of using RSM is to determine the optimum values of the independent variables in order to attain the highest COD and turbidity removal efficiencies. For this purpose, the analyses of the models (Eq(3) and Eq(4)) obtained by the CCD design were used. The optimum values of the independent variables obtained for the maximum COD and turbidity removal were 5.8, 241.36 A/m², and 29.19 min for initial pH, current density and electrolysis time, respectively. Furthermore, when EC experiments were run using the optimum values of the operating parameters (obtained from synthetic COE studies) on both synthetic and spent COE, the results were respectively: 97.42 %, 94.35 % for COD and 99.97 %, 99.93 % for turbidity. While, the predicted removal efficiencies using the obtained equations were 98.42 % for COD and 100% for turbidity. After running EC experiments using the obtained optimal conditions, the results indicated a very good agreement with the predicted removal efficiencies.

4. Biodegradability of COE

Cumulative methane production curves, from pretreated and non-pretreated, synthetic and spent COE, representing the variation of the cumulative methane yield as a function of time are shown in Figure 1. It should be noted that the methane production was calculated after subtracting the inoculums production share.
Results show an exponential increase of the cumulative methane production for the pretreated COE, however for the non-pretreated samples the exponential variation can be noticed at the beginning of the experiments for the first two days only. Afterwards the production became low and almost no methane yield was observed.

In fact, the results show that the cumulative methane yields reached 0.024 ± 0.007 for the non-pretreated synthetic COE after 150 days, 0.094 ±0.04 Nm^3 CH_4 kg COD^{-1} for the non-pretreated spent COE after 150 days, 0.175 ± 0.05 Nm^3 CH_4 kg COD^{-1} for the pretreated synthetic after 28 days and 0.27 ± 0.01 Nm^3 CH_4 kg COD^{-1} for the pretreated spend COE after 16 days.

Pretreated samples showed the highest cumulative methane production with an improvement of 650 % and 187 % for synthetic and spent COE respectively.

These results indicate effectively that EC pretreatment enhanced methane yield considerably. In fact, the pretreated COE yields are near the theoretical stoichiometric value of 0.35 Nm^3 CH_4 kg COD^{-1}. Moreover, they are very close to those reported by (Perez et al., 2006), when anaerobic thermophilic co-digestion of COE was used with a methane yield reaching 0.27 Nm^3 CH_4 Kg COD^{-1}. However when COE wastewater samples were used solely, by the authors, a lower methane yield was obtained (0.001 Nm^3 CH_4 Kg COD^{-1}).

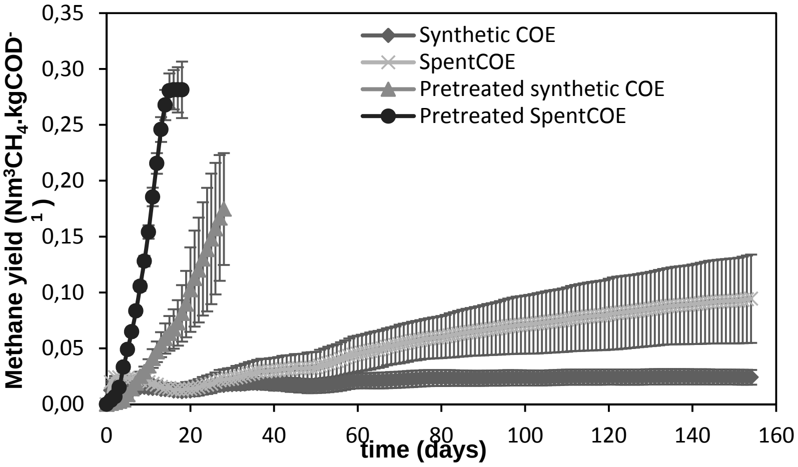

Figure 1: Cumulative methane production.

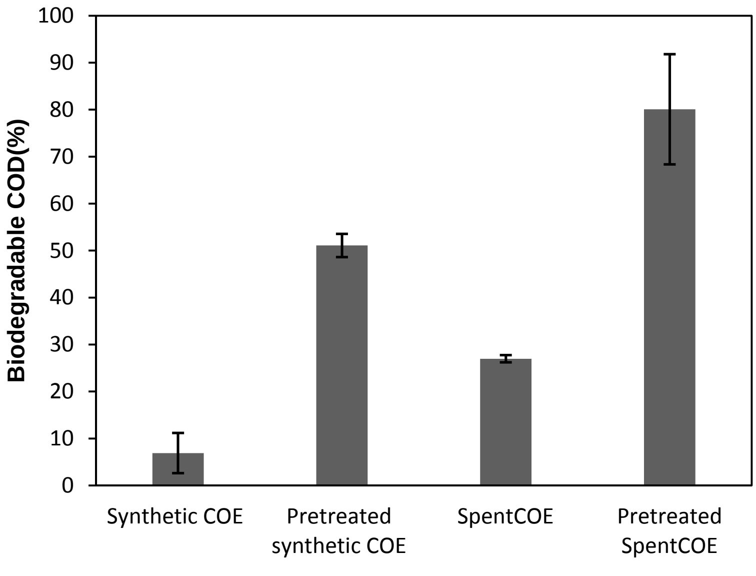

Figure 2: anaerobic biodegradability of the COE.

In order to assess the effect of EC pretreatment on biodegradability, the anaerobic biodegradability was determined using the following equation (Buffiere et al., 2008):

$$\%\, Biodegradability = \frac{BMP \times 10^{-3}}{0.35} \times 100 \quad (5)$$

Where (BMP) is the biochemical methane potential calculated as the ratio of the produced methane volume to the introduced COD expressed by (Nm^3 CH_4 Kg COD^{-1}); (0.35 Nm^3 CH_4 Kg COD^{-1}) is the theoretical maximum methane yield under standard conditions of temperature and pressure (0 °C; 1.013 x 10^5 Pa).

The results of the biodegradability reported in Figure 2 show the positive effect of the EC pretreatment on the COE AD treatment. The biodegradability increased from 6.9 to 51 % and from 26.98 to 80 % for synthetic and spent COE respectively. The results show a considerable improvement in biodegradability due to electrocoagulation effects, most probably, on chemicals bonds within COE macro-molecules which helps in breaking them into smaller ones.

5. Conclusions

This study demonstrated the benefits resulting from using EC in COE pretreatment prior to AD process. The combination of EC and AD in treating COE resulted in an enhancement in biogas production and COD removal by 650 % and 187 % as well as in reducing the incubation time.

Moreover, experimental design methodology was used to find the optimal conditions for EC pre-treatment which were 5.8 for initial pH, 241 A/m^2 for Current density and 29 min for processing time, to achieve 97.42 % and 94.35 % COD removal efficiency and 99.97 % and 99.93 % turbidity removal efficiency for synthetic and spent COE, respectively.

At the end, the results presented in this paper demonstrate the success and the competitiveness of the EC pretreatment prior to AD in the treatment of COE.

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