

EFFECTS OF DIRECT AND ALTERNATING CURRENT ON THE TREATMENT OF OILY WATER IN AN ELECTROFLOCCULATION PROCESS

A. A. Cerqueira, P. S. A. Souza and M. R. C. Marques*

Instituto de Química, Laboratório de Tecnologia Ambiental, Universidade do Estado do Rio de Janeiro, UERJ, Rio de Janeiro - RJ, Brasil.

Phone: + (55) (21) 2334-0159, Fax: + (55) (21) 2334-0159 CEP: 20550-013
E-mail: monicamarques@uerj.br

(Submitted: October 23, 2012 ; Revised: October 19, 2013 ; Accepted: October 19, 2013)

Abstract - In the direct current mode (DC), widely used in electroflocculation (EC), the formation of an impermeable oxide layer on the cathode causes the declining of the efficiency of this process. This disadvantage has been reduced by adopting alternating current (AC). In this study, the effects of AC and DC on operational parameters such as the removal of oils and greases (O&G), color and turbidity from oil-in-water (O/W) emulsions of the petroleum industry using aluminum electrodes were investigated. Removal efficiencies of 95%, 97% and 99% of O&G, color and turbidity with energy consumption of 0.280 kWh/m³ and electrode consumption of 0.12 g and 0.18 g were achieved at a current density of 3 A, operation time of 3 minutes and initial pH of 9.0 using AC and DC, respectively. In continuous flow tests performed with the same experimental conditions, the electrode consumption at times up to 60 minutes were 1.6 g and 3.4 g using AC and DC, respectively.

Keywords: Electroflocculation; Petroleum industry; Produced water; Alternating current; Direct current.

INTRODUCTION

Produced water, one of the main problems in the petroleum industry, is generated in increasing volumes from both old and new wells (Campos *et al.*, 2005). This effluent represents 98% of all wastewater generated in the petroleum industry. This water contains complex organic and inorganic substances, such as salts, metals, dispersed oil and dissolved hydrocarbons and also presents high temperature and the absence of oxygen (Thomas, 2004).

Therefore, produced water is an important source of pollutants and, as the environmental laws have become stricter, the cost of its treatment has become

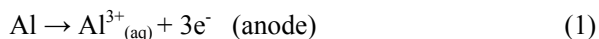
increasingly high. This fact has led to many efforts to find more effective and less expensive ways to treat this water (Li *et al.*, 2009).

The treatment of produced water applies a primary treatment to separate the floatable oils from the water and emulsified oils. This treatment process usually involves retaining the oily wastewater in a holding tank, while allowing gravity separation of the oily material, which is subsequently skimmed from the wastewater surface. Meanwhile, a secondary treatment phase is then required to break the oil-water emulsion and separate the remaining oil from the water. Emulsions may be broken by chemical, physical, or electrical methods. Chemical meth-

*To whom correspondence should be addressed

ods are the most widely used in this treatment. However, these chemical methods present troublesome filtration processes, providing an incentive to explore other alternatives (Yang, 2007).

In recent years, electrocoagulation (EC) of synthetic or real oily water has been investigated by some researchers (Ruback and Saur, 1997; Dórea *et al.*, 2007; Tir and Mostefa, 2008; Canizares *et al.*, 2007; Benzadok *et al.*, 2008; Asselin *et al.*, 2008; Abdelwahaba *et al.*, 2009; Ramalho *et al.*, 2010; Lima *et al.*, 2009; Cerqueira *et al.*, 2011). During electrolysis, four main mechanisms generally occur simultaneously: (a) electrolytic reactions at the electrode surfaces, (b) formation of coagulant agents in the aqueous phase, (c) adsorption of soluble or colloidal pollutants by these agents and (d) removal by sedimentation or flotation. Aluminum is released from the anode (reaction 1) and hydrogen gas is formed at the cathode (reaction 2):



The aluminum chemical reaction in water is very complex, because aluminum is capable of forming several compounds, such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}(\text{OH})_4^-$, as well as polymeric species like $\text{Al}_6(\text{OH})_{15}^{3+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_8(\text{OH})_{20}^{4+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, $\text{Al}_{13}(\text{OH})_{34}^{5+}$, which are finally transformed into $\text{Al}(\text{OH})_3$ according to complex precipitation kinetics (Gurses *et al.*, 2002; Rebhun and Larue, 1993).

The advantages of electrocoagulation include high particulate removal efficiency, a compact treatment facility, relatively low costs and the possibility of complete automation. This method is characterized by reduced sludge production, a minimum requirement of chemicals and easy operation (Chen, 2004; Vasudevan *et al.*, 2011).

In the direct current (DC) technology, widely used in EC, the anode oxidation causes the formation of an impermeable oxide layer on the cathode, which increases the resistivity of the electrode. With the time, the efficiency of the EC process declines. This problem can be minimized by addition of sacrificial electrodes in a parallel configuration in the electrolytic cell (Yousuf *et al.*, 2001; Cerqueira *et al.*, 2009). Furthermore, to reduce the cathode passivation and to extend the lifetime of the electrodes, the direction of current at regular intervals of time can be manually inverted. Thus, cathode and anode can be switched periodically. However, many researchers have preferred the use of alternating current in

the EC process. It is assumed that the cyclic energization between the anode–cathode in an alternating current (AC) system simulates the manual reversion of polarity. It delays the cathode passivation and anode deterioration and thus ensures reasonable electrode life (Vasudevan *et al.*, 2011).

Eyvas *et al.* (2009) investigated the effects of alternating current (AC) on dye removal from aqueous solutions by electrocoagulation (EC). An EC system with parallel-connected aluminum electrodes was operated in batch mode. Two different aqueous dye solutions were used. The experiments employing direct current (DC) were carried out using a DC power supply. The AC experiments were conducted using a rectangular wave, which is produced with an adjustable time relay connected to the output of a DC power supply. This current was called alternating pulse current (APC) in order to refer to the AC system in this study. Total organic carbon (TOC) and dye removal efficiencies were measured to assess treatment efficiency. The results of this study showed that high removal efficiencies of TOC and dye can be acquired in shorter operation times by using an APC system (5 min of operation time).

Keshmirizadeh *et al.* (2011) showed that electroflocculation (with Fe/Al electrodes) could be applied in the treatment of industrial effluents containing Cr^{6+} . The alternating pulse current (APC) mode was found to be more efficient than the DC mode with a lower anode over-voltage, slower anode polarization and passivity, and lower tank voltage. The operating time was 3–25% less when the APC mode was used, based on an initial Cr^{6+} concentration of 50–1000 mg/L, respectively. Because of the reduction in operating time, less power (or energy) is consumed, which makes the APC mode more cost effective. Application of APC eliminates uneven wear (dissolution) of electrodes. Typically, the anode material dissolves and electroreduction products stick to the cathode when the DC mode is used. In this study, water recovery was found to range from 0.7 to 0.92, based on initial Cr^{6+} concentrations from 50 to 1000 mg/L, respectively.

Vasudevan *et al.* (2011) investigated the effects of AC and DC on the removal of cadmium from water using aluminum electrodes as anode and cathode. The results showed that removal efficiencies of 97.5 and 96.2% with energy consumptions of 0.454 and 1.002 kWh m^3 were achieved at a current density of 0.2 A/dm² and pH of 7.0 using aluminum alloy electrodes and AC and DC, respectively. The aluminum hydroxide generated in the cell reduced the cadmium concentration in water to less than 0.005 mg/L

and made it suitable for drinking. The results indicate that the process can be scaled up to higher capacity.

The electrocoagulation with the AC process was compared to the chemical coagulation process for the treatment of oily waste generated by the petroleum industry (Cerqueira *et al.*, 2011). From the results, one may conclude that this EC process was effective for the effluent studied, while chemical coagulation was not successful.

The main objective of this study was to investigate the effects of AC and DC treatment using aluminum electrodes as anode and cathode in order to evaluate the decrease of turbidity, color and oil and grease content (O&G) from a synthetic oil/water (O/W) emulsion. Important electrochemical factors were investigated such as: initial pH, current density, distance between electrodes and electrocoagulation time.

EXPERIMENTAL

Synthetic Oil/Water (O/W) Emulsion

To simulate produced water, a synthetic oil/water (O/W) emulsion was prepared in a 2 L beaker containing 1 g of crude oil (from the Campos Basin, Rio de Janeiro state, Brazil, with density 0.89 g/L and 28 °API), 0.1 g/L of the emulsifiers SP-60[®] and TW-60[®] (1:1 ratio - Oxiteno Corp.) and 0.9 L of distilled water salinized with synthetic sea salt (60 g/L – Coralife Corp.). This mixture was then subjected to vigorous mechanical stirring at 10,000 rpm (Wigen Hauser D-500 homogenizer) for 10 minutes to form a stable O/W emulsion. Table 1 shows the characteristics of the emulsified oily wastewater.

Table 1: Characteristics of simulated oily wastewater.

Parameter	Values
Color ($A_{400\text{ nm}}$)	2.3 – 2.9
Turbidity (NTU)	4100 – 4750
pH	7.9 – 9
Conductivity (mS/cm)	98 – 100.7
O&G (mg/L)	650 - 690

Electrocoagulation Experimental Set-Up

Batch Reactor

A monopolar electrode with two pairs of aluminum plates (10 cm x 5 cm x 0.3 cm) was placed vertically in a 1.5 L beaker. The interelectrode distance

was variable at 0.5 to 2.0 cm. The runs were performed using both AC and DC sources and at ambient temperature (25 °C). The pH was adjusted to the desired value using NaOH or H₂SO₄. All tests were performed in triplicate and kept under stirring at 200 rpm. The weight loss of the electrodes was evaluated after cleaning, drying and weighing each electrode in order to assess the best operational conditions. Between the tests, the electrolytic cell (including the electrodes) was cleaned with 5% (v/v) hydrochloric acid solution for at least 15 min and then rubbed with a sponge and rinsed with tap water.

Continuous Flow Reactor

In a 5 L supply tank, kept under continuous agitation to assure that the effluent was emulsified, a peristaltic pump (Exata, EX 20 SV) was connected to allow flow control with pre-determined times to feed the electrolytic cell. This cell consisted of a 1.8 L glass tank with four deflectors in which monopolar electrodes were vertically inserted with 4 pairs of aluminum plates (10 cm x 5 cm x 0.3 cm) and separated by spacers 1.0 cm thick each. The electrode mass consumption was determined by cleaning, drying and weighing each electrode before and after each test. The time interval samples were taken from the reactor at 10th, 20th, 30th, 40th, 50th and 60th minutes of the treatment times. All assays were performed in triplicate. Both AC and DC current were used. In the DC electroflocculation tests, the polarity was reversed every 5 minutes (Figures 1 and 2). After 30 min, the effectiveness of each parameter was determined by the differences in turbidity, color and O&G content between treated and untreated emulsions. Before the analysis, the treated solutions remained for 30 min without stirring for separation of the oily material.

Description of Alternating Current and Direct Current Electrocoagulation

All tests, batch or continuous flow reactor, were conducted with two electrolytic units: DC and variable frequency AC. The DC electroflocculation unit (15 V) was composed of a voltage inverter plugged into a standard AC outlet (127 V/60 Hz), then connected in line to a step-down transformer feeding a bridge rectifier, responsible for providing DC to the electrodes through a polarity reversing switch, with a voltmeter and ammeter to measure the parameters of the electrodes (Figure 1). The tests were carried out at current densities of 1, 2, 3, 4 and 5 A.

The AC unit had an output of 15 V and frequency of 60 Hz between 1 and 120 Hz, obtained from an AC/AC frequency converter (Manufacturer WEG, Model: CFW0800) connected to and a voltage step-down transformer (Tecnopeltron model PLTN 100/15), again with a voltmeter and ammeter to read the parameters. This allowed converting the 60 Hz frequency from the power grid into variable frequency output from 1 to 120 Hz (Figure 2). In this study, all tests were carried out with a frequency of 60 Hz (Cerqueira *et al.* 2011).

Analytical Methods

The process efficiency was measured in terms of the following parameters: color, turbidity, and oils & greases (O&G), which were measured by the procedure described in *Standard Methods for the Examination of Water and Wastewater* (APHA, 2005). O&G measurements were performed with a Soxhlet

extractor (5520D) and the remaining color was evaluated by measurements of absorbance of the solutions at a wavelength of 400 nm. The equipment used was a Femto 600S spectrophotometer. The turbidity tests were performed with a Tecnopon TB 1000 turbidimeter. Conductivity was measured with a Digimed DM3 conductivimeter and pH, adjusted with 3 mol L⁻¹ H₂SO₄ solution, was measured with an Oakton ION 6 Acon Series pH meter.

Energy Consumption (E_c)

The energy consumption was calculated by Eq. (3):

$$E_{C_{kWh/m^3}} = \frac{V \cdot i \cdot t}{v} \quad (3)$$

where V is the operating voltage (volt), i is the operating current (ampere), t (or t_{E_c}) is the time of reaction (min) and v is the volume of effluent (m³).

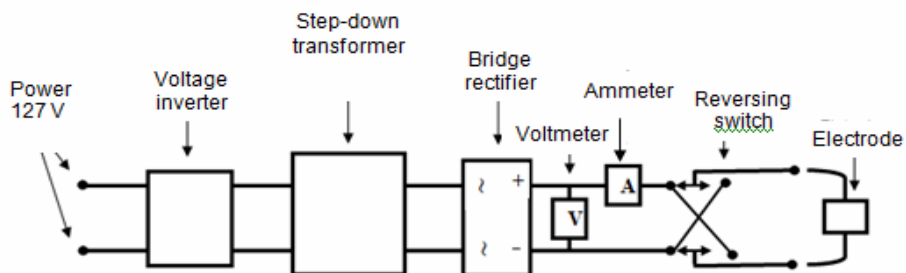


Figure 1: Schematic diagram of the experimental DC electroflocculation unit.

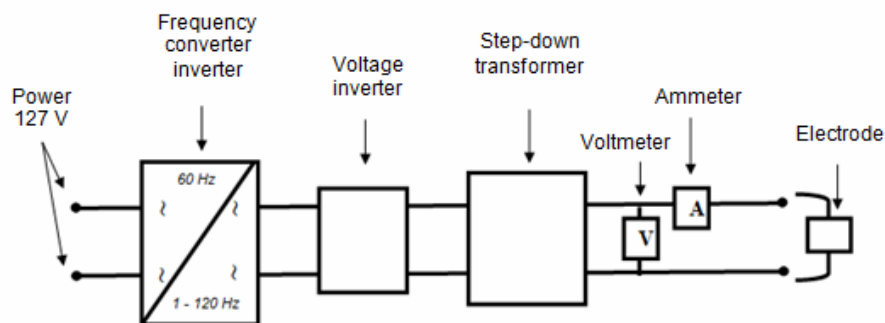


Figure 2: Schematic diagram of the experimental AC electroflocculation unit.

RESULTS AND DISCUSSIONS

Influence of Operating Parameters on the Electroflocculation Process

Among the most important characteristics of the oil-in-water emulsion are the high turbidity and oil & grease content (O&G). The turbidity of an emulsion is related to the concentration of droplets, so that it can be used to determine the oil concentration in the emulsion. In addition, turbidity also depends on the size of the oil droplets and, as the droplets tend to coalesce, the turbidity may decrease, due to a lower number of droplets or an increase in their size. Then, the important parameters which affect the efficiency of oil removal by the electrocoagulation process are: current density, initial pH, interelectrode distance and electrolysis time.

Effect of Current Density

The amount of O&G removal depends on the quantity of flocculation agent (aluminum hydroxide) generated, which is related to the time and current density. To investigate the effect of current density on the O&G removal, a series of experiments were carried out on solutions containing 690 mg/L, at pH 9.0 with current density varying from 1 to 5 amperes in 3 minute time periods using both the AC and DC current source.

The results demonstrated that the removal efficiency of O&G showed no statistically significant differences and that the energy consumption was lower in the case of AC than with DC at current densities higher than 3 A, (Table 2). Therefore, the results shown indicated that the use of the AC mode of electroflocculation promoted a lower electrode consumption as compared to when using DC under all

conditions tested, probably due to the uniform dissolution of the anode and cathode during electrocoagulation when using the AC mode.

In this study, the high conductivity of the O/W emulsion (around 100.7 mS/cm) caused a very low voltage (~ 2.0 V) for a current density of 3 A in both technologies. The increase in conductivity of the effluent favors electrical current conduction, reducing the voltage between the electrodes, and consequently requiring less energy for the electrolytic process.

According to Daneshvar *et al.*, (2004), higher electrical current density increases the dissolution of the anode, producing a larger quantity of coagulation agent generated in a fixed time. The presence of coagulant in solution contributes to an increase in oil removal efficiency by flotation of the oil droplets, reduction of electrostatic repulsion between the air bubble and oil droplets and an increase of oil droplet hydrophobicity. Moreover, the rate of generation of bubbles increases and the bubble size decreases. These effects are favorable for destabilization of the emulsion. The effect of current density on the final removal efficiency of chemical oxygen demand (COD) upon increasing the applied power was also observed by Bensadok *et al.* (2008), Khemis *et al.* (2005) and Kobya *et al.* (2006).

In the present investigation, a current density around 3 A seems to be enough for a better electrolytic flocculation for both AC or DC sources and consequently a maximum efficiency of removal (99% turbidity, 97% color and 94% O&G).

Since increasing the applied current density means a higher energy consumption, the current density of 3 amperes (A) was selected for the next experiments using the DC source, because increasing the density did not improve the removal efficiencies of O&G, color and turbidity.

Table 2: Effect of current density (CD) on the removal efficiency of O&G, energy and electrode consumption using AC and DC. Initial O&G, 690 mg/L; conductivity, 100,7 μ S/cm and initial pH, 9.0.

CD (A)	AC			DC		
	Removal efficiency (%)	Energy consumption (kWh/m ³)	Electrode consumption (kg/m ³)	Removal efficiency (%)	Energy consumption (kWh/m ³)	Electrode consumption (kg/m ³)
1	81.0 \pm 2.0	0.09 \pm 0.01	0.07 \pm 0.01	75.8 \pm 3.1	0.07 \pm 0.01	0.11 \pm 0.01
2	91.0 \pm 1.7	0.18 \pm 0.01	0.09 \pm 0.01	90.3 \pm 2.1	0.17 \pm 0.01	0.15 \pm 0.02
3	94.3 \pm 0.6	0.28 \pm 0.00	0.12 \pm 0.10	94.1 \pm 0.6	0.28 \pm 0.02	0.18 \pm 0.10
4	92.7 \pm 0.6	0.38 \pm 0.04	0.15 \pm 0.20	93.5 \pm 0.6	0.46 \pm 0.03	0.22 \pm 0.20
5	93.7 \pm 0.6	0.48 \pm 0.10	0.18 \pm 0.20	94.2 \pm 0.6	0.69 \pm 0.10	0.26 \pm 0.30

Influence of Initial pH

It has been established that the initial pH is an important parameter in determining the performance of the electrocoagulation process. In order to examine the effect of pH on the removal efficiencies of turbidity, color and O&G, the pH was varied between 4 and 9. The maximum removal was at pH above 6 in the electrocoagulation process using the DC source: 96% O&G, 99% turbidity and 99% color (Figure 3). These results are similar to those obtained in previous studies using an AC source by Cerqueira *et al.*, (2011). However, in this case, at pH 5 the efficiency was lower than with the DC source: 61% O&G, 6% turbidity and 37% color. In both processes (AC or DC) the removal remained unchanged until pH 9. Experiments at pH above 9 were not performed because it is known that the flocs of aluminum hydroxide are less reactive and the flocculation is less effective. Nevertheless, there was good removal efficiency at neutral pH. This result is an advantage of electrolysis for the treatment of produced water, considering that this type of effluent generally has pH between 7 and 9 (Queiroz *et al.*, 1996).

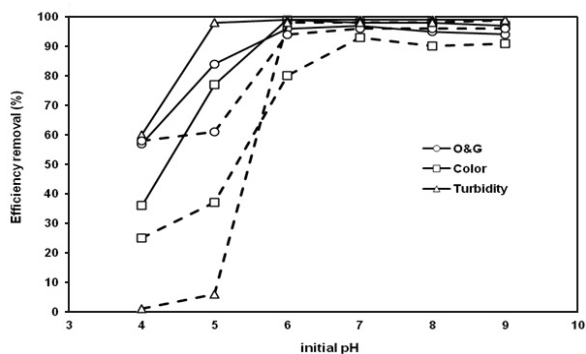


Figure 3: Effect of initial pH on color, turbidity and O&G with the DC source (—) and the AC source (---). Conditions: current intensity 3A, time lapse: 3 min., interelectrode distance: 0.5 cm, oil concentration: 690 mg/L, conductivity: 100.7 uS/cm, initial pH: 9.0, color: 2.9 abs, turbidity: 4750 NTU, temperature: 25 °C and emulsifier: 100 mg/L.

A comparison of the turbidity test results showed that, with pHs of 4 and 5, removal occurred only slightly with the AC source. For the DC source at initial pH 4, the removal was 60% and at pH 5 it was 98%. One hypothesis to explain this difference is that, with AC, at the beginning of the aluminum oxidation there is no formation of the minimum amount of coagulant required to treat the effluent in this pH range. In the case of DC, the electrode

oxidation is probably higher since, even when the pH is not optimal for coagulation, there is greater formation of flocculating factors. From pH 6 to 9, both AC and DC behave alike in the removal parameters analyzed, since in this pH range there is formation of the primary flocculating agent $Al(OH)_3$. Therefore, because the pH of this oily water was 9, it was selected for the next experiments.

Effect of Interelectrode Distance

The interelectrode distance is an important variable in order to optimize the operating costs of electrolysis systems. Researchers report that when the conductivity of the effluent is high, a larger spacing between the electrodes is possible. On the other hand, when conductivity is low, the spacing should be smaller (Crespilho and Rezende, 2004).

In this study, the interelectrode distance (4 aluminum electrodes in the cell) was varied from $d = 0.5$ to 2.0 cm while the other factors remained unmodified. In Figure 4, the removal efficiencies for all parameters were above 90% for the DC source, indicating that the inter-electrode distance did not greatly affect the performance. These results are similar to those obtained in the electrocoagulation using the AC source under the same conditions by Cerqueira *et al.* (2011).

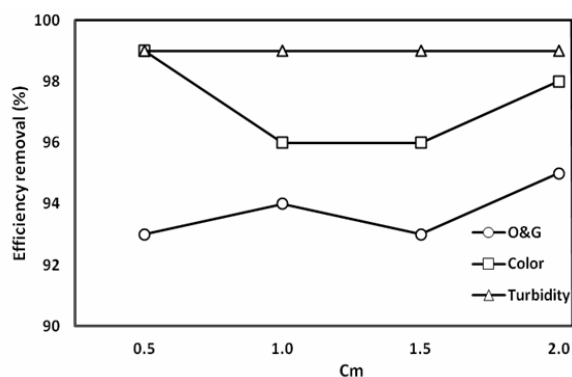


Figure 4: Effect of interelectrode distance on removing color, turbidity and O&G. Experimental conditions: initial pH 9, time 3 min., Current intensity 3 A, DC source, oil concentration: 690 mg/L, conductivity: 100.7 uS/cm, initial pH: 9.0, color: 2.9 abs, turbidity: 4750 NTU, temperature: 25 °C and emulsifier: 100 mg/L.

When the distance between electrodes increases, the energy consumption also increases due to the higher resistivity of the solution (Den and Huang, 2005). The results in Figure 4 showed no improve-

ment in the efficiency of reduction of the parameters for distances between the electrodes greater than 0.5 cm using a current density of 3 A, indicating that this is the optimal distance since the use of larger distances would involve greater energy consumption (0.5 cm = 1.95V; 2.0 cm = 3.00V).

Effect of Time

Regarding the time, experiments were carried out at pH 9 for an initial O&G concentration of 690 mg L⁻¹ in the presence of 60 g L⁻¹ NaCl. The variation in the O&G removal considering the electrolysis time for oily wastewater at different current densities revealed that, using higher current densities, the oil removal is faster. The direct influence of the electrical current density on the time and the kinetics of removal of pollutants was also observed in previous studies (Chen *et al.*, 2000; Kumar *et al.* 2004; Mouedhen *et al.*, 2008).

The results presented in Figure 5 show the effect of variation of the electrolysis time (1 to 5 min) on the efficiency of O&G, color and turbidity removals at a current density of 3 A with the DC source. It appears that turbidity, color and O&G exhibit regular variations with a more continuous increase with time reaching a constant value. This behavior may be due to destabilization of the emulsion.

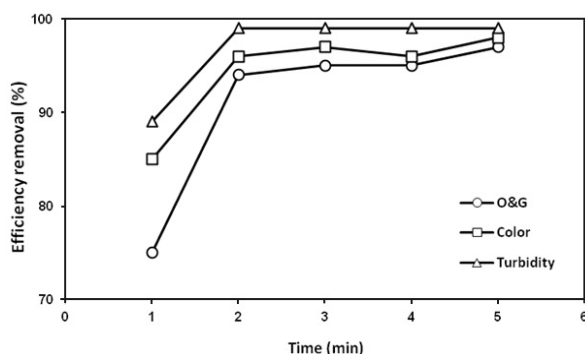


Figure 5: Effect of variation of time on removing color, turbidity and O&G. Experimental conditions: initial pH 9; current intensity 3 A, interelectrode distance 0.5 cm, DC source, oil concentration: 690 mg/L, conductivity: 100.7 uS/cm, color: 2.9 abs, turbidity: 4750 NTU, temperature: 25 °C and emulsifier: 100 mg/L.

The first 1 min of the electrocoagulation using the DC source gave a considerable removal of turbidity and color (above 85%) of the initial emulsion. The increase in the electrolysis time gave better results for the removal efficiencies reaching 99% turbidity,

97% color and 95% O&G, after just 2 min. However, with an increase of the electrolysis time, the removal efficiency remains constant and the emulsion becomes visually very clear. These results are similar to those obtained by Cerqueira *et al.* (2011) when an AC source was used under the same conditions (99% turbidity, 95% color and 96% O&G).

Electrolytic Treatment in Continuous Flow

Experiments were carried out in a continuous flow unit of 5 L capacity and contact times of 2, 4, 6, 8, 10 and 12 minutes per liter. After verifying the viability of the wastewater treatment by the electrolytic process with alternating current and direct current at low residence times in the system, the practicability of operation under continuous flow was checked. Figure 6 shows the efficiency of electrolysis as a function of time for AC and DC.

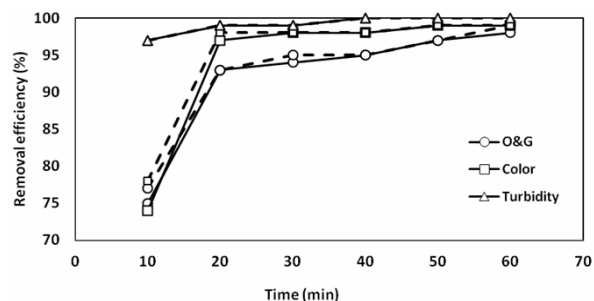


Figure 6: Removal efficiency of the indicated parameters after electroflocculation with DC (—) and AC (---). Conditions: initial pH 9, interelectrode distance 1 cm and current intensity 3 A, oil concentration: 690 mg/L, conductivity: 100.7 uS/cm, color: 2.9 abs, turbidity: 4750 NTU, temperature: 25 °C and emulsifier: 100 mg/L. Each test performed with 5 L of effluent.

A similarity in the removal was observed under the same conditions of AC and DC. Twenty minutes of electrolysis was enough for the removal with efficiencies above 90%. After this period, the further removal of an additional 5% is not justified by the higher consumption of electricity and electrodes.

Figure 7 shows the aluminum electrode weight loss by oxidation using the alternating current and direct current sources as a function of time in the continuous flow electrolysis.

After 10 minutes of AC electrolysis, the consumption of the aluminum electrode was 0.27 g and the consumption in DC was 0.4 g, whereas in 60 minutes of electrolysis the consumptions were 1.6 g and 3.4 g in AC and DC, respectively. Therefore, DC

consumes the electrode much faster, meaning that AC performs better.

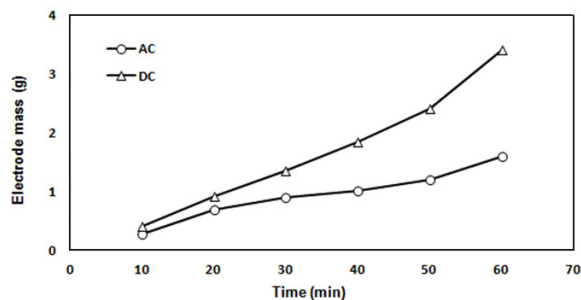


Figure 7: Aluminum electrode weight loss by oxidation by AC and DC for different electroflocculation times in continuous flow electrolysis.

One hypothesis for the higher electrode consumption by DC in relation to AC is that, because DC current flows in one direction, it may cause irregular wear on the electrode plates due to the oxidation at the same preferential points of the electrode. In the case of AC, the reversal of current probably wears the electrodes more uniformly and allows a longer life.

CONCLUSIONS

In this study, the efficiency of the electroflocculation process applied to the treatment of oily wastewater emulsion was investigated with alternating current and direct current.

It was observed that the electroflocculation treatment achieves a fast and effective removal of turbidity, color and oil and greases. The treatment efficiency was found to be a function of the initial pH, interelectrode distance, applied current density and electrolysis time under the optimal values of the process parameters.

The results showed removal efficiencies of 94%, 97% and 99% of O&G, color and turbidity with an energy consumption of 0.280 kWh/m³ with electrode consumption of 0.12 g and 0.18 g could be achieved at a current density of 3 A with an operation time of 3 minutes and initial pH of 9.0 using AC and DC, respectively.

Continuous flow tests performed under the same experimental conditions showed that the consumptions of electrodes with time up to 60 minutes of electroflocculation were 1.6 g and 3.4 g using AC and DC, respectively.

Therefore, the results indicated that the use of the AC mode of electroflocculation promoted a lower

electrode consumption as compared to using DC under all conditions tested. This technique thus seems to be a promising alternative for the treatment of oil-in-water (O/W) emulsions of the petroleum industry.

ACKNOWLEDGEMENT

We thank the Foundation for the Coordination for Improvement of Higher Education Personnel (CAPES), National Council for Scientific and Technological Development (CNPq) and the Research Foundation of the State of Rio de Janeiro (FAPERJ) for financial support. This study is part of the project INOG (Brazilian National Institute of oil and gas).

REFERENCES

- Abdelwahaba, O., Aminb, N. K., El-Ashtoukhyb, E. Z., Electrochemical removal of phenol from oil refinery wastewater. *J. Hazard. Mat.*, 163, p. 711-716 (2009).
- APHA-AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater. 21st Ed., American Public Health Association, Washington, DC (2005).
- Asselin, M., Drogui, P., Brar, S. K., Benmoussa, H., Blais, J., Organics removal in oily bilgewater by electrocoagulation process. *J. Hazard. Mat.*, 15, p. 1446-455 (2008).
- Bensadok, K., Benammar, S., Lapicque, F., Nezzal, G., Electrocoagulation of cutting oil emulsion using aluminum plate electrodes. *J. Hazard. Mat.*, 152, p. 423-430 (2008).
- Campos, A. L. O., Rabelo, T. S., Santos, R. O., Melo, R. F. L. V., Cleaner production in the oil industry: The case of the water produced in the field of Carmópolis/SE. 23, ABES (2005).
- Cañizares, P., Martínez, F., Lobato, Rodrigo, J. M. A., Break-up of oil-in-water emulsions by electrochemical techniques. *J. Hazard. Mat.*, 145, p. 233-240 (2007).
- Cerqueira, A. A., Marques, M. R. C., Russo, C., Evaluation of alternating current electrolytic process for treating produced water. *Quim. Nova*, 34, p. 59-63 (2011).
- Cerqueira, A. A., Russo, C., Marques, M. R. C., Electroflocculation for textile wastewater treatment. *Braz. J. Chem. Eng.*, 26, 4, p. 659-668 (2009).
- Chen, G., Electrochemical technologies in wastewater treatment. *Sep. Purif. Technol.*, 3, p. 11-41 (2004).

- Chen, G., Chen, X., Yue, P. L., Electrocoagulation and electroflotation of restaurant wastewater. *J. Environ. Eng.*, 126, p. 858-863 (2000).
- Crespilho, F. N. and Rezende, M. O. O., *Electroflocculation: Principles and Applications*. São Carlos, Rima (2004).
- Daneshvar, N., Sorkhabi, H. A., Kasiri, M. B., Decolorization of dye solution containing Acid Red 14 by electrocoagulation with a comparative investigation of different electrode connections. *J. Hazard. Mat.*, 112, p. 55-62 (2004).
- Den, W. and Huang, C., Electrocoagulation for removal of silica nano-particles from chemical-mechanical-planarization wastewater. *Colloids Surfaces A: Physicochem. Eng. Aspects*, 254, p. 381-389 (2005).
- Dórea, H. S., Bispo, J. R. L., Aragão, K. A. S., Cunha, B. B., Navickiene, S., Alves, J. P. H., Romão, L. P. C., Garcia, C. A. B., Analysis of BTEX, PAHs and metals in the oilfield produced water in the state of Sergipe, Brazil. *Microchem. J.*, 85, p. 234-238 (2007).
- Eyvaz, M., Kirlaroglu, M., Aktas, T. S., Yuksel, E., The effects of alternating current electrocoagulation on dye removal from aqueous solutions. *Chemical Engineering Journal*, 153, p. 16-22 (2009).
- Gürses, A., Yalçın, M., Doğar, C., Electrocoagulation of some reactive dyes: A statistical investigation of some electrochemical variables. *Waste Manag.*, 22, p. 491-499 (2002).
- Keshmirizadeha, E., Yousefia, S., Rofouei, M. K., An investigation on the new operational parameter effective in Cr(VI) removal efficiency: A study on electrocoagulation by alternating pulse current. *J. Haz. Mat.*, 190, p. 119-124 (2011).
- Khemis, M., Tanguy, G., Leclerc, J. P. G., Valentin, L., Lopicque, F., Electrocoagulation for the treatment of oil suspensions: Relation between the rates of electrode reactions and the efficiency of waste removal. *Proc. Saf. Environ. Protect.*, 83, p. 50-57 (2005).
- Kobyas, M., Hiz, H., Senturk, E., Aydinler, C., Demirbas, E., Treatment of potato chips manufacturing wastewater by electrocoagulation. *Desalination*, 190, p. 201-21 (2006).
- Kumar, P. R., Chaudhari, S., Khilar, K. C., Mahajan, S. P., Removal of arsenic from water by electrocoagulation. *Chemosphere*, 55, p. 1245-1252 (2004).
- Li, G., Guo, S., Li, F., Treatment of oilfield produced water by anaerobic process coupled with micro-electrolysis. *J. Environ. Science*, 22, p. 1875-1882 (2009).
- Lima, R. M. G., Wildhagen, G. R. S., Cunha, J. W. S. D., Afonso, J. C., Removal of ammonium ion from produced waters in petroleum offshore exploitation by a batch single-stage electrolytic process. *J. Hazard. Mat.*, 161, p. 1560-1564 (2009).
- Mouedhen, G., Feki, De Petris Wery, M., Ayed, H. F., Behavior of aluminum electrodes in electrocoagulation process. *J. Haz. Mat.*, 150, 1, p. 124-135 (2008).
- Queiroz, M. S., Souza, A. D., Abreu, E. S. V., Gomes, N. T., Neto, O. A. A., *Aplicação do Processo Eletrolítico ao Tratamento de Água de Produção*. CENPES-DITER-SEBIO, RT, Rio de Janeiro, Brazil (1996). (In Portuguese).
- Ramalho, A. M. Z., Huitle, C. A. Silva, D. R., Application of electrochemical technology for removing petroleum hydrocarbons from produced water using a DSA-type anode at different flow rates. *Fuel*, 89, p. 531-534 (2010).
- Rebhun, M. and Lurie, M., Control of organic matter by coagulation and floc separation. *Water Sci. Technol.*, 27, p. 1-20 (1993).
- Rubach, S., and Saur, I. F., Onshore testing of produced water by electroflocculation. *Filtrat. Sep.*, 34, p. 877-882 (1997).
- Thomas, J. E., *Fundamentals of Petroleum Engineering*. 2nd Ed. Rio de Janeiro, Interciência (2004).
- Tir, M. and Mostefa, N., Optimization of oil removal from oily wastewater by electrocoagulation using response surface method. *J. Hazard. Mat.*, 158, p. 107-115 (2008).
- Vasudevan, S., Lakshmi, J., Sozhan, G., Effects of alternating and direct current in electrocoagulation process on the removal of cadmium from water. *J. Hazard. Mat.*, 192, p. 26-34 (2011).
- Yang, C., Electrochemical coagulation for oily water demulsification. *Sep. Purif. Tech.*, 54, p. 388-395 (2007).
- Yousuf, M., Mollah, A., Schennach, R., Parga, J. R., Cocke, D. L., *Electrocoagulation (EC): Science and applications*. *J. Hazard. Mat.*, 84, p. 29-41 (2001).