

Electrochemical treatment of Produced Water using Ti/Pt and BDD anode

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The applicability of electrochemical oxidation (EO) to treat a real petrochemical effluent was investigated using a lab electrochemical cell and pre-pilot plant scale reactor with Ti/Pt and BDD anode materials. The efficacy of EO in treating a real effluent was determined and the reactors compared at different applied current densities ($j = 15, 30$ and 60 mA cm^{-2}). The results clearly indicate that an electrochemical pre-pilot reactor removes more than 97% of dissolved organic matter applying 15 mA cm^{-2} at pH 6.0 and 25°C after 30 min of electrolysis, consuming 3.37 kWh m^{-3} , and incurring a cost of around 0.57 USD m^{-3} . The results obtained provide valuable information regarding the EO scaling-up process, aimed at applying electrochemical technologies to treat actual effluents on a real scale.

Keywords: produced water, platinum, wastewater treatment, anodic oxidation, diamond electrode.

1. INTRODUCTION

Electrochemical technologies are considered a promising alternative to enhance water quality by eliminating persistent hazardous contaminants. Electrochemical advanced oxidant processes (EAOPs) are the most important techniques to promote mineralization of highly persistent organic

pollutants (POPs) via direct or indirect electrochemical approaches [1-4]. Novel electrosynthetic approaches are of particular interest for technical innovations and future industrial applications because they enable the direct use of electricity to generate valuable compounds or oxidant species (e.g.: reactive oxygen species or active chlorine species). The combination with other approaches in organic and physical chemistry allows the establishment of powerful synthetic tools aimed at green chemical processes [5-6].

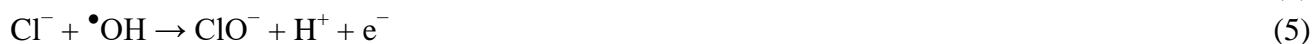
Electrochemical oxidation (EO) is the most popular EAOP, where the existence of direct (by direct charge transfer at the anode (M) or mediated electrochemical reactions (by strong oxidants such as reactive oxygen species (ROS) and/or active chlorine species) makes it possible to remove organic pollutants from the effluents [1,2].

Mediated electrochemical transformations in the absence of chloride occur by electrogenerated ROS [1,7,8], mainly the hydroxyl ($\bullet\text{OH}$) radical, which is produced by water oxidation on the anodal surface (reaction (1)) [1,2].



Thus, complete combustion is favored due to the non-selective attack of organic pollutants, but the concentration of $\bullet\text{OH}$ depends on the electrocatalytic nature of electrodes, which determines the interaction of these oxidants on their surfaces (chemically or physicochemically adsorbed).

In the second case, mediated electrochemical reactions (in the presence of chloride) promote the production of Cl_2 (reaction 2) and active chlorine species such as HClO and ClO^- (reactions 3-5), by Cl^- ion oxidation on the anode [4,9,10], but oxidant production efficiency and the predominance of these species in solution depend on the pH of the effluent [4].



The production of active chlorine species using specific electrode materials, such as dimensional stable anodes (DSA) or boron-doped diamond (BDD) films, highlights the possible usage of EO technology [9] when the Cl^- ion is present in the effluent. Moreover, the production of chlorate and perchlorate ions (toxic chlorine species) can be avoided by employing BDD or DSA electrocatalytic materials with a specific composition and suitable operating conditions [11,12].

Water pollution by the petrochemical industry is a worrisome environmental issue [13]. The volume of produced water (PW) associated with oil and natural gas exploration/production varies during fluid extraction, but can reach 100% by the end of the useful life of the well [14, 15]. The final exploration activities in the basin aim to maximize oil extraction by injecting water, causing substantial production of water contaminated with dissolved/suspended solids, organic compounds and heavy metals [16]. Several treatments can be applied to treat PW, including chemical or biological methods,

and the use of membranes and advanced oxidation processes [17-19]. However, as indicated above, significant PW production restricts the applicability of these technologies.

Several research groups have published reports that demonstrate the applicability of different electrochemical treatments in removing petroleum hydrocarbons from wastewater [20-29]. For example, Yavuz and co-workers [26] investigated the applicability of different EOAPs in treating petroleum refinery wastewater (PRW). Boron-doped diamond (BDD) and/or ruthenium mixed metal oxide (Ru-MMO) electrodes were used to study IEO and EO, and the electro-Fenton (EF) process using iron electrodes was also investigated. Electrochemical oxidation (EO) achieved higher removal efficiencies (99.53 and 96.04%) for phenol and organic matter, respectively, in terms of chemical oxygen demand (COD), at 5 mA cm⁻² with the BDD anode, while 94.5% phenol and 70.06% COD removal was obtained at 20 mA cm⁻², demonstrating the effective oxidation of organic pollutants using diamond anodes [26]. When a real petrochemical effluent was treated using BDD electrodes, adding an established amount of NaCl (0.05 M), 98.9% phenol and 95.48% COD removal was achieved after 90 min at a current density of 3 mA cm⁻² due to the electrogeneration of active chlorine species [26]. Conversely, 98.74% phenol removal was obtained after 6 min of electrolysis and 75.71% COD removal after 9 min of electrolysis using the EF process [26], considered the most efficient method, followed by EO using a BDD anode.

Moreno and collaborators [30] also investigated the EF process for the electrochemical remediation of oil extraction wastewater using the iron anode. The authors obtained the best COD reduction (74.8%) in a sample after 1 h at 3.5 mA cm⁻² [11], but the slow rate of COD reduction could be attributed to secondary reactions involving O₂, Cl₂ and H₂ evolution. Moreover, Ramalho and co-workers [25] examined the efficiency of EO in depolluting PW using a flow reactor with a Ti/RuO₂-TiO₂-SnO₂ anode at 89 mA cm⁻². The results showed that different flow rates (0.25, 0.5, 0.8 and 1.3 dm⁻³ h) achieved 98, 97, 95 and 84% dissolved organic matter removal. However, poor elimination of ethyl benzene and phenol occurred, with 17-47% at 0.25, 0.5, 0.8 dm⁻³ h and 20-47% at 0.25, 0.8 and 1.3 dm⁻³ h, respectively. Rocha and collaborators [31] studied the treatment of PW by EO with Ti/Pt and BDD anodes in a batch electrochemical cell. The results showed that 98% COD removal was achieved applying 60 mA cm⁻² with a BDD due to the efficient production of hydroxyl radicals and persulfate. Conversely, in the Pt electrode, 80% COD removal was reached under similar experimental conditions. Silva and coworkers [32] treated different petrochemical effluents (fresh, brine and saline) with Ti/IrO₂-Ta₂O₅ and BDD electrodes in a flow reactor.

In the case of fresh PW, organic matter was poorly eliminated (approximately 84%) when Ti/IrO₂-Ta₂O₅ was used. By contrast, complete depolluting was achieved in the BDD anode at 5 mA cm⁻². Higher mineralization efficiency was obtained using BDD (90%) compared to 30% at Ti/IrO₂-Ta₂O₅. For brine PW, complete COD removal was achieved applying 30 mA cm⁻² at Ti/IrO₂-Ta₂O₅, after 240 min of electrolysis, while at lower current densities (10 and 20 mA cm⁻²), 71.5% and 78.6% COD removals were obtained, respectively. For the BDD anode, total decontamination of the effluent was achieved at all current densities, markedly decreasing electrolysis time, due to the electrochemical production of active chlorine species. Mineralization efficiency ranged from 92 to 99%.

In 2014, the electrochemical treatment of petrochemical wastewater with Ti/Pt and BDD anodes and Ta/PbO₂ and BDD electrodes was reported by Santos and colleagues [33] and Gargouri

[34], respectively. Results clearly indicated that organic matter degradation (in terms of COD) was achieved in Ti/Pt and BDD anodes applying 20, 40 and 60 mA cm⁻². In the former, 64.5 90.7 and 93.6% of COD was removed at 20, 40 and 60 mA cm⁻². However, 76.2, 94.5 and 97.1% COD removal was obtained after 8 h of treatment, in the latter electrode. For the bulk experiments performed by Gargouri coworkers [34], BDD was the most efficient electrocatalytic material, degrading 96% of organic matter, while 85% COD removal was observed at Ta/PbO₂ applying 30 mA cm⁻².

Given that scaling up from the laboratory to full scale is an important issue in electrochemical technology, in addition to its efficacy in removing recalcitrant compounds from water using different anodes in pilot plants [25-26,30-34], the development of electrochemical water reactors to depollute industrial effluents is an important alternative to explore. In this respect, the novelty of the present study is based on the depuration of a real petrochemical effluent using Ti/Pt and BDD anodes in a lab electrochemical cell on a pre-pilot plant scale at 15, 30 and 60 mA cm⁻² to compare two systems and evaluate their depollution efficacy.

2. MATERIALS AND METHODS

2.1 Chemicals

The petrochemical effluent was provided by the oil industry located in Rio Grande do Norte state (northeastern Brazil); the effluent was subjected to filtration prior to treatment in order to avoid suspended solids. Produced water was characterized and physicochemical parameters are reported in Table 1. Chloride and sulfide were analyzed using American Public Health Association (APHA) procedures. Chemical oxygen demand (COD) was determined after chloride concentration decreased using the precipitation method with AgNO₃.

Table 1. Characteristics of the real petrochemical effluent before treatment.

Parameter	value
Salinity	1440 g Kg ⁻¹
Total solids	2223 mg L ⁻¹
Resistivity	361.0 Ω cm
CO ₃	21048 mg L ⁻¹
pH	6.7
Conductivity	2.8 mS cm ⁻¹
Sulfite	4.57 mg L ⁻¹
Chloride	6200 mg L ⁻¹
HCO ₃	203288 mg L ⁻¹
Density	0.974 g cm ⁻³
Suspended solids	836 mg L ⁻¹
Total dissolved solids	1387 mg L ⁻¹
Chemical oxygen demand	4600 mg L ⁻¹
Alkalinity	166.63 mg L ⁻¹

2.2. Electrolytic systems

An undivided electrochemical cell (Fig. 1) or pre-pilot electrochemical reactor (Fig. 2) was employed to carry out the bulk experiments, respectively. In the first case, a 0.5 L reaction section is the main part of the cell where 15 cm² square electrodes (geometrical area) were used. The real wastewater (1 L in a batch reservoir) was continuously recirculated through the flow reactor on a pre-pilot scale at 310 L h⁻¹ in the second case. Fig. 1 illustrates the flow cell containing an electrolytic compartment with a 1.2 cm interelectrode gap between the 63.5 cm² electrodes. Ti/Pt was acquired from DeNora Electrodes (Italy) and BDD was purchased from METAKEM GmbH (Usingen, Germany), which were used as anodes. The experiments were galvanostatically performed using a DC-MPL 3305M power supply, applying 15, 30 and 60 mA cm⁻².

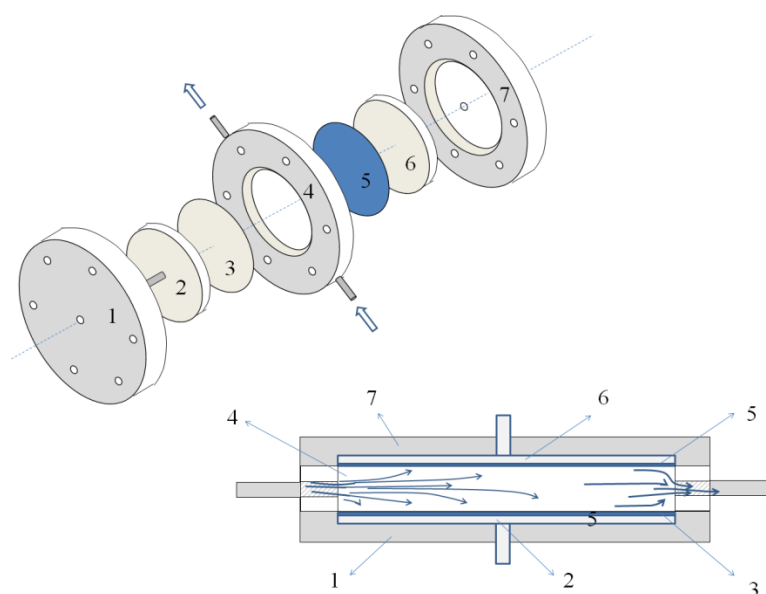


Figure 1. Filter-press electrochemical cell reactor: (1) anodic part, (2) electric contact, (3) Nb/BDD or Ti/Pt electrode, (4) electrolytic compartment (76.2 cm³), (5) cathode: Ti plate, (6) electric contact and (7) cathodic part.

2.3. Apparatus and analytical procedures

The solution pH was measured and adjusted on a Tecnal pH-meter. COD concentrations were determined with HANNA COD kit tests (range 0–15000 mg L⁻¹) and a HANNA HI 83099 COD photometer, after the digestion procedure. COD abatement was estimated using the expression below (6) [35]:

$$\% \text{ COD} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100 \quad (6)$$

where COD_0 and COD_t , given in $g\ O_2\ dm^{-3}$, are the initial COD of the effluent and the COD at time t , respectively. Absorbance ($Ab_{S_{max}}$) was determined at $\lambda = 300\ nm$ using an Analytic Jena SPECORD 210 PLUS UV-vis spectrophotometer due to the absorbance of aromatic pollutants in PW.

3. RESULTS AND DISCUSSION

3.1. Electrochemical treatment in a conventional electrochemical cell

Figure 2 depicts the absorbance measurements, as a function of time, in Ti/Pt and BDD anodes used to treat PW effluent by EO at different current densities applied for 120 min. When the Ti/Pt anode was used, the absorbance of the effluent exhibited slight variations at the end of the treatment compared with the BDD anode, which showed a significant increase in absorbance during batch electrochemical cell electrolysis.

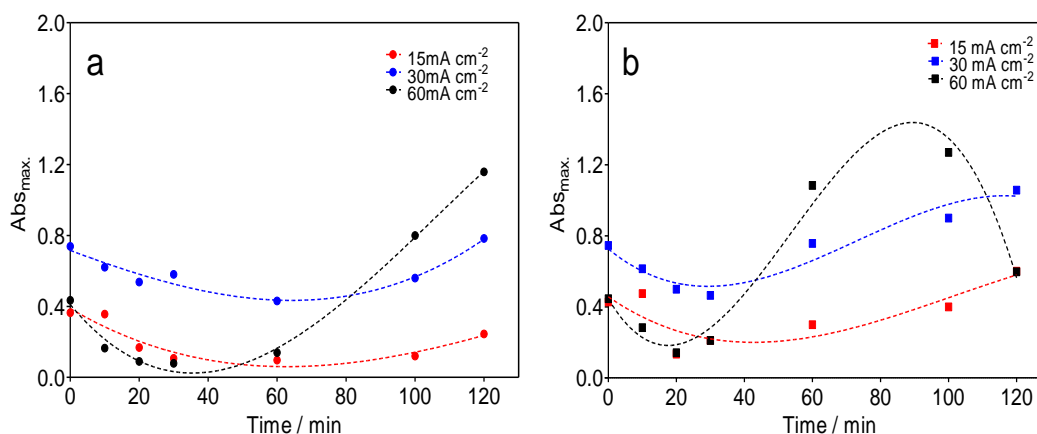


Figure 2. Absorbance measurements vs electrolysis time in the electrochemical treatment of 0.5 L of PW at pH 6.0 and 25 °C at different applied current densities using (a) Ti/Pt or (b) BDD anodes.

This trend indicates the presence of aromatic compounds in the effluent, since they are oxidized, generating by-products during electrolysis. These compounds absorbed radiation via the chromophore groups in their structure. However, this behavior is more evident in the BDD electrode at higher applied current densities. Subsequent conditions strongly depend on the oxidative pathway followed by the electrocatalytic nature of the material (Ti/Pt or BDD). Thus, organic matter eliminated during electrolysis must be determined in order to understand the efficacy of the treatment process under the operating conditions used.

As discussed by other researchers [25-26, 30-34], according to the environmental regulations of several countries, effluent discoloration does not indicate the complete elimination of contaminants because other intermediates could be colorless. As such, it is essential to measure the organic load in the effluent [1-4]. Figures 3a and b illustrate the elimination of dissolved organic matter (in terms of COD) in PW and the percent of organic matter removed (insets) by EO after 120 min at different applied current densities. Results indicate that decontamination of the PW effluent was performed at

different levels, depending on the electrocatalytic material used. In the Ti/Pt, organic matter was poorly eliminated because parallel reactions can be preferentially favored (reactions (7-9)), mainly oxidation of $\bullet\text{OH}$ to O_2 (7), H_2O_2 production by reaction (8) or oxygen evolution reaction (9) [3,35,36].



At 15 mA cm^{-2} , 82% COD removal was achieved. However, efficiency declined at 30 mA cm^{-2} , which could be related to oxygen evolution. An increase in efficacy was subsequently achieved, but this may be associated with the production of active chlorine species on the Ti/Pt surface due to the high Cl^- content in the effluent, prompting a slight increase in COD removal (Fig. 3a).

Conversely, in the BDD anode, organic mineralization [23,37] rose when j increased from 15 to 60 mA cm^{-2} , causing an increase in COD removal from 67.0 to 99.0% (Fig. 3b). This behavior assumes that the electrical charge in the cell was efficiently employed when BDD was used and j increased.

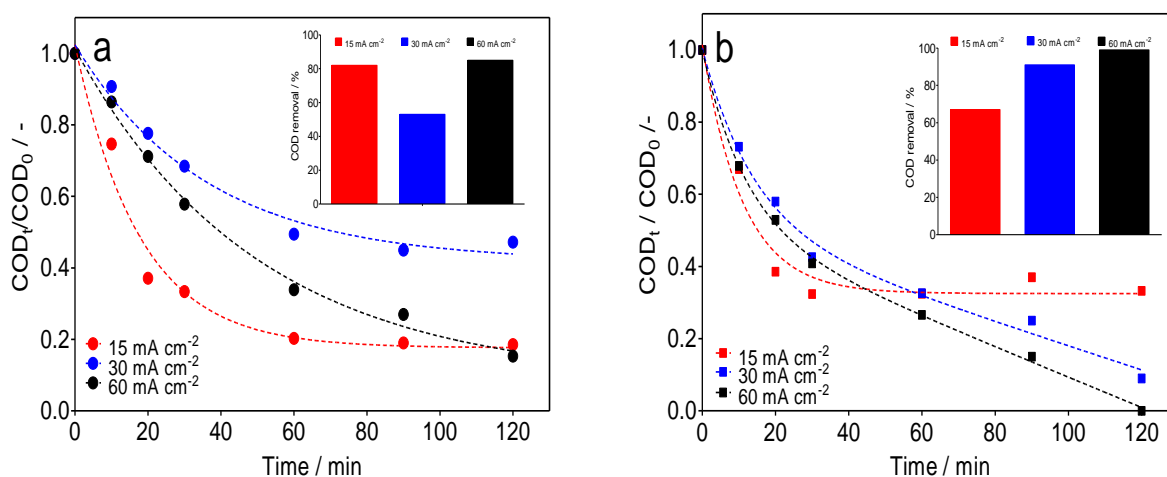


Figure 3. Percentage of COD removal achieved after 120 min of EO treatment of 0.5 L of PW effluent at pH 6.0 and $25 \text{ }^\circ\text{C}$ with (a) Ti/Pt or (b) BDD anodes, applying 15, 30 and 60 mA cm^{-2} .

In both cases, the efficiency of the process is associated with enhanced $\bullet\text{OH}$ generation (reaction 1); however, EO efficacy using the BDD anode may also be related to the electroconversion of chloride into active chlorine species by reactions (2-5) or the participation of $\bullet\text{OH}$ in producing these oxidant species (reactions (10-12)).



Fig 3b shows that COD decreased by 91% when 30 mA cm^{-2} was applied. By contrast, only 53% COD removal was achieved under the same experimental conditions with Ti/Pt. These results indicate that active chlorine species contribute to the oxidization of organic compounds [2, 38, 39], but organo-chlorinated compounds can be feasibly generated. Thus, mineralization efficiency declines because these species are more recalcitrant and not as easily oxidizable as the initial contaminants in the effluent [9,11].

3.2. Electrochemical treatment in a electrochemical cell reactor

The hydrodynamic configurations of an electrochemical reactor as well as j are the most important conditions that influence process efficiency, kinetics and the extent of the reactions. As such, the hydrodynamic conditions of the reactor improve mass transport, while j controls electrochemical $\bullet\text{OH}$ generation and active chlorine species, to a greater or lesser extent. Fig. 4 depicts a change in the electrochemical setup and an increase in j , causing important variations in the absorbance values recorded in both electrodes. In the case of Ti/Pt, more radiation-absorbing intermediates are produced in the effluent at j values of 15 and 30 mA cm^{-2} after 120 min of electrolysis. For the BDD anode, a significant by-product production was achieved at all j values, but absorbance decreased at the end of the EO treatment, indicating that the intermediates are transformed into simpler organic compounds. This trend shows that, due to the increase in j , the oxidants produced on the BDD surface react with the organic pollutants in the effluent, lowering overall absorbance values. In the Ti/Pt electrode, parasitic reactions may be favored, decreasing process efficiency (reactions 7-9).

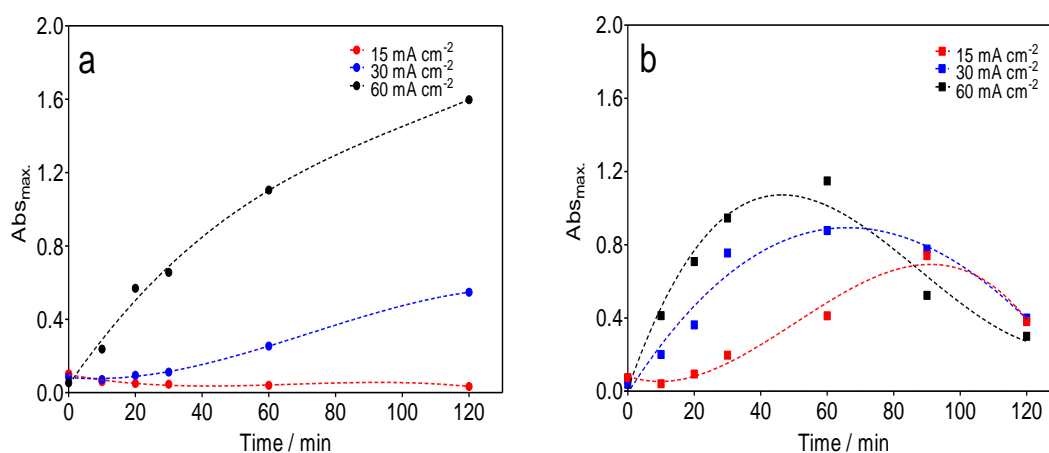


Figure 4. Absorbance measurements vs electrolytic time in the electrochemical treatment of the PW effluent (1 L) at pH 6.0 and $25 \text{ }^\circ\text{C}$ using (a) Ti/Pt or (b) BDD anodes at different applied current densities.

On the other hand, if the BDD anode favors the production of active chlorine species, decolorization by homogeneous oxidants is faster than that obtained by heterogeneous $\bullet\text{OH}$, as discussed above. Nevertheless, electrogeneration of active chlorine species seems to be limited by the applied j and electrocatalytic properties of the anode material. Although a noticeable improvement in the pollutant removal from PW effluents can be expected by absorbance measurements when a BDD anode is used, COD reduction must be determined to understand the efficacy of the flow cell in conducting electrochemical incineration of the pollutants into CO_2 and water [1-4]. Fig. 5a and b illustrate the applicability of the flow cell in reducing COD using Ti/Pt and BDD electrodes at different j . Results showed that different PW wastewater elimination performance was achieved using an electrochemical flow cell reactor with both electrocatalytic materials than that recorded with a conventional electrochemical cell. Indeed, different COD decays were obtained in the Ti/Pt anode (Fig. 5a), exhibiting a greater decrease in COD concentration with increasing j (36%, 67% and 96% applying 15, 30 and 60 mA cm^{-2} , respectively). The oxygen evolution reaction was likely limited due to the liquid flow injected into the reactor, and a higher concentration of $\bullet\text{OH}$ was electrogenerated by reaction (1), promoting the elimination of organic pollutants, mainly at 30 and 60 mA cm^{-2} . Thus, the hydrodynamic configuration of the electrochemical reactor improved the electrochemical treatment of PW wastewater. However, COD removal was slightly lower using an electrochemical flow cell (Figure 5a) compared to a conventional cell (Figure 3a) when j was 15 mA cm^{-2} . Indeed, 82% was estimated for the former and 36% for the latter, in the Ti/Pt anode. The loss in efficiency is due to parasitic (7-8) and oxygen evolution reactions (9), which reduce $\bullet\text{OH}$ generation and the mineralization of organic compounds.

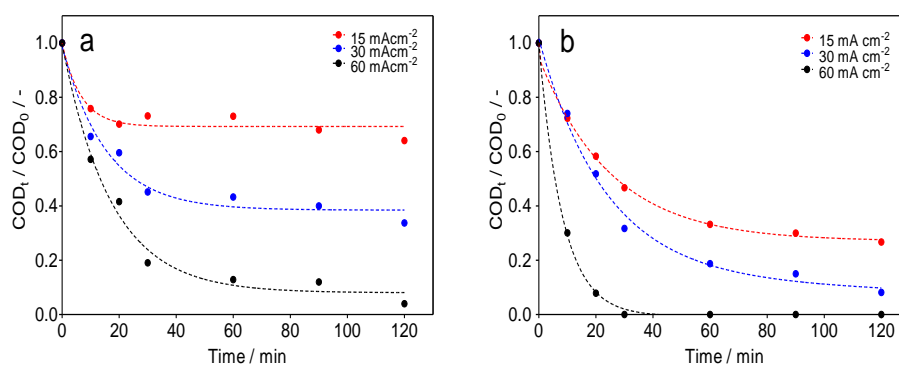


Figure 5. COD removal achieved after 120 min of electrochemical treatment of 1 L of PW at pH 6.0 and 25 °C applying different j : (a) Ti/Pt or (b) BDD anodes.

As previously discussed, j plays a significant role in organic pollutant degradation using a flow reactor with a BDD anode because an increase in j promotes a rapid COD reduction over short treatment times (Fig. 5b). Results demonstrated that EO efficacy increased using the electrochemical flow cell due to the efficient electrogeneration of oxidants, such as $\bullet\text{OH}$ and active chlorine. COD removal of 74 and 92% was obtained at 15 and 30 mA cm^{-2} , respectively, which was significantly higher than that achieved under the same experimental conditions using the conventional cell (67% and 91% at 15 and 30 mA cm^{-2} , respectively, see Fig. 3b). Based on these results, we can conclude

that, in addition to improving organic pollutant elimination in the PW effluent, hydrodynamic conditions also contribute to treating larger volumes.

3.3. Energy requirements

In order to justify the electrochemical treatment as an alternative to treat petrochemical effluents, it is important to determine energy consumption requirements, which are directly associated with operating conditions (j , electrode material, supporting electrolyte, and so on). Operating costs were then calculated based on these estimations. Next, EC (in kWh m⁻³) was estimated using equation (13) [37,40]:

$$EC = \frac{\Delta E_c I t}{1000 V_s} \quad (13)$$

Where ΔE_c is average cell voltage in V and V_s the volume treated in m³. Electrical requirements and costs are reported in Table 2. Treatment cost was estimated using the Brazilian electrical energy price per kWh (BRL 0.625, excluding taxes), which was then converted into USD. As can be observed, EC is proportional to j , and therefore to cost, when the batch reactor was used with Ti/Pt and BDD anodes and the flow pre-pilot reactor with the Ti/Pt electrode to treat the real effluent. However, when the flow cell was employed with the BDD electrode, lower EC requirements were achieved than those estimated for the pre-pilot cell with Ti/Pt, in addition to higher COD removals. Unfortunately, the costs of EO technology remain higher than those associated with conventional effluent treatments, and an alternative would be the use of renewable energy sources, such as solar panels [41,42] or windmills [43].

Table 2. EC and operational costs to electrochemically treat PW in batch and pre-pilot flow reactors using different anodes after 2 h of electrolysis.

Experimental conditions		Energy consumption (kWh m ⁻³)		Costs (USD m ⁻³)	
Anode	j (mA cm ⁻²)	Batch cell	Flow cell	Batch cell	Flow cell
Ti/Pt	15.0	0.78	6.21	0.13	1.05
	30.0	2.21	15.84	0.37	2.67
	60.0	4.84	29.76	0.82	5.03
BDD	15.0	5.70	3.37	0.96	0.57
	30.0	17.10	10.35	2.88	1.75
	60.0	78.00	7.08 ^a	13.17	1.19

^a value determined after 30 min due to the rapid elimination of organic matter.

Thus, taking into account all the results reported here, the use of an electrochemical flow cell with a BDD anode in EO at 15 mA cm⁻² could be an alternative in the treatment of petrochemical

effluents, allowing higher organic matter abatements at reasonable costs, followed by biological post-treatment.

The relevant results obtained with electrochemical technologies for treating petrochemical effluents are summarized in Table 3, and compared with the figures obtained in this work. As can be observed, the efficiencies achieved, in terms of COD removal, are comparable with other electrochemical technologies, corroborating the significant mineralization achieved with different anodes. However, the lower energy requirements evidence the feasibility of EO as an alternative treatment of real effluent generated by petrochemical industry.

Table 3. Degradation of organic compounds present in the PW by electrochemical treatments [17-19]

EAOP	Anode	j (mA cm ⁻²)	Electrolysis time (h)	COD removal (%)	Pollutant removal (%)	Treated volume (mL)	EC (kWh dm ⁻³)	Ref.
IEO	BDD	3.0	1.5	95.46	Phenol 98.90	300	- ^a	[26]
EF	iron	3.5	1.0	74.80	- ^a	1800	- ^a	[30]
EF	iron	1.0	0.15	75.71	Phenol 98.74	300	- ^a	[26]
EO	Ru-MMO	20.0	3.5	70.06	Phenol 94.50	300	- ^a	[26]
	BDD	5.0	5.0	96.04	Phenol 99.53		4.05 (kWh g ⁻¹)	
	RuO ₂ - TiO ₂ - SnO ₂	89.0	0.5	>84%	Phenol 30 Benzene 82 Toluene 100 Ethyl benzene 92 <i>o</i> -, <i>m</i> -, <i>p</i> - Xylene 100	5000	- ^a	[25]
	Ti/Pt BDD	60	10	80 98	- ^a	500	139.52 109.80	[31]
	Ti/IrO ₂ - Ta ₂ O ₅ BDD	5	2	84 100	TOC 30 TOC 90	1000	- ^a	[2]
	Pt/Ti BDD	40	8	90.7 94.5	- ^a	5000	140 191	[33]
	Ta/PbO ₂ BDD	30	11 8	85 96	- ^a	200	46.6 38.0 (kWh m ⁻³)	[34]
	Pt/Ti BDD	60	2	84.0 99.0	- ^a	500	4.84 ^b 78.0 ^b	This work

							(kWh m ⁻³)	
	Pt/Ti BDD	60	2 0.5	96.0 100.0	- ^a	1000	29.76 ^c 7.08 ^c	This work

^a = Not determined, ^b = batch cell, ^c = flow cell.

4. CONCLUSIONS

The use of a flow reactor to depollute petrochemical effluents is a promising technology to reduce the environmental impacts of discharging PW in aquatic systems. The hydrodynamic conditions of this system make it possible to efficiently produce oxidant species in the effluent to act as oxidized mediators in the bulk solution. Although absorbance measurements provide a general indication of electrochemical efficacy, the decline in COD achieved at the end of the treatment demonstrates the effectiveness of this approach. The range of j shows that 15 mA cm⁻² is an optimum operating condition to achieve satisfactory abatement of organic pollutants after 30 min using BDD anodes and the electrochemical pre-pilot cell reactor, with affordable costs of 0.57 USD m⁻³, treating a more significant volume of effluent than the batch reactor. These promising results encourage the development of new electrochemical treatment studies on a pre-pilot plant scale using alternative electrocatalytic materials to treat actual effluents.

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