

Applicability of Electrochemical Oxidation Process to the Treatment of Petrochemical Effluents

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Electrochemical technologies are a promising alternative for the treatment of wastewaters containing organic pollutants. The main advantages of these processes include environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation and cost effectiveness. However, the effectiveness of the electrochemical approaches depends strongly on electrode materials and cell parameters (mass transport, current density, water composition, etc.). Then, the use of high performance anodic materials can achieve high efficiency and lower the operating cost. Therefore, several research groups are recently studying the applicability of the electrochemical technologies for treating real domestic and industrial effluents, with the aim of that a diversification of techniques must be sought, adapting the treatment to each situation, as much as possible. In this context, this work presents the results concerning to the application of electrochemical technologies to treat petrochemical effluents, emphasizing the new results obtained concerning to the use of direct and indirect electrochemical oxidation processes as an alternative to pollution abatement of effluents generated by Brazilian petrochemical industries.

1. Petrochemical industry

1.1 Produced water

The significance of oil and natural gas in modern civilization is well known. The process of refining crude oil consumes large amounts of water. Consequently, significant volumes of wastewater are generated. Oilfield wastewater or “produced water (PW)” contains various organic and inorganic components that can pollute surface and underground water and soil (Ahmaduna et al., 2009). The volume of petroleum refinery effluents generated during processing is 0.4–1.6 times the amount of the crude oil processed (Abidin, 2009). Thus, based on the current yield of 84 million barrels per day (mbpd) of crude oil, a total of 33.6 mbpd of effluent is generated globally (Coelho et al., 2006). World oil demand is expected to rise to 107 mbpd over the next two decades, and oil will account for 32% of the world’s energy supply by 2030, while biofuels (including ethanol and biodiesel) are expected to account for 5.9 mbpd by 2030, and the contributions from renewable energy sources like wind and solar power are estimated to be 4–15% (Diya’uddeen et al., 2011; Marcilly, 2003). These data clearly indicate that effluents from the oil & gas industry will continually be produced and discharged into the world’s main water bodies. As regards the significant matter of environmental concern, many countries have implemented more stringent regulatory standards for discharging PW. On the other hand, because large volumes of PW are being generated, many countries with oilfields, which are also generally water-stressed countries, are increasingly focusing on efforts to find efficient and cost-effective treatment methods to remove pollutants as a way to supplement their limited fresh water resources.

Naturally occurring stones in subsurface formations are generally permeated by different underground fluids such as oil, gas, and saline water. Before trapping hydrocarbon compounds in rocks, they were saturated with saline water. Hydrocarbons with lower density migrated to trap locations and displaced some of the saline water from the formation. Finally, reservoir rocks absorbed saline water and

hydrocarbons (oil and gas). There are three sources of saline water: (i) flow from above or below the hydrocarbon zone, (ii) flow from within the hydrocarbon zone and (iii) flow from injected fluids and additives resulting from production activities (Ahmaduna et al., 2009).

The last category is called "connate water" or "formation water" and becomes "PW" when saline water mixed with hydrocarbons comes to the surface (Ahmaduna et al., 2009; Veil et al., 2004). In oil and gas production activities, additional water is injected into the reservoir to sustain the pressure and achieve greater recovery levels. Both formation water and injected water are produced along with hydrocarbon mixture. At the surface, processes are used to separate hydrocarbons from the produced fluid or PW. Then, PW is considered to be one of the largest waste streams in the petroleum, oil and gas industry. Effects of PW components on the environment are: (i) increase in the salinity, (ii) dispersed and soluble oil contribution in marine ecosystems, (iii) inclusion of other compounds from treating chemicals, (iv) higher concentration of heavy metals than in seawater and (v) presence of radionuclides.

PW characteristics depend on the nature of the producing/storage formation from which they are withdrawn, the operational conditions, and chemicals used in process facilities. The composition of PWs from different sources can vary by order of magnitude. However, PW composition is qualitatively similar to oil and/or gas production (Ekins et al., 2007). The major compounds of PW include: (i) Dissolved and dispersed oil compounds (a mixture of hydrocarbons including benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene, phenanthrene, dibenzothiophene (NPD), polyaromatic hydrocarbons (PAHs) and phenols), (ii) Dissolved formation minerals, (iii) Production chemical compounds (include some chemicals that are added to treat or prevent operational problems), treatment chemicals (production treating, gas processing, and stimulation) and production treating chemicals (scale and corrosion inhibitors, biocides, emulsion breakers, antifoam), (iv) Production solids (including solids formation, corrosion and scale products, bacteria, waxes, and asphaltenes) and (v) Dissolved gases. Water cannot dissolve all hydrocarbons, so most of the oil is dispersed in water; and dissolved and suspended oil present in PW (prior to treatment) depend on several factors (Ahmaduna et al., 2009; Fillo et al., 1992).

1.2 PW treatment

Considerable studies have been conducted to investigate new treatment technologies in order to treating PW. An extensive literature reporting the characteristics and applications of most important conventional technologies developed for this purpose including physical-chemical and chemical methods, advanced oxidation processes (AOPs), microbiological treatments and biological decomposition, has been collected in an authoritative review (Ahmaduna et al., 2009). Ahmaduna et al. (2009) have indicated that oil content and salinity of PW from offshore and onshore activities can be reduced through various physical, chemical, and biological methods. In offshore extraction facilities due to space constraints, compact physical and chemical treatment technologies are preferred. However, as capital cost of physical methods and cost of chemicals for chemical treatment of hazardous sludge is high, the application of these methods is limited. Current methods cannot remove minute suspended oil and/or hazardous dissolved organic and inorganic components. In contrast, biological treatment is a cost-effective method for removing dissolved and suspended compounds from oilfield wastewater in onshore extraction facilities. Nevertheless, electrochemical technologies for destroying petrochemical pollutants from PW have showed great attention in the last years (Hansen and Davies, 1994; Rajkumar and Palanivelu, 2004; Santos et al., 2006; Lima et al., 2009; Ramalho et al., 2010; Rocha et al., 2012; Santos et al., 2013; Silva et al., 2013; Santos et al., 2014). Therefore, a general overview of lab and pilot plant experiments related to the most relevant applications of electrochemical methods for removing petroleum hydrocarbons from PWs will be presented.

2. 5. Applicability of electrochemical technologies for treating petrochemical effluents

Few reports have been published by Brazilian researchers concerning the application of electrochemical technologies for treatment of petrochemical effluents (Hansen and Davies, 1994; Rajkumar and Palanivelu, 2004). Northeastern Brazilian research groups are recently working in the applicability of these electrochemical technologies due to this region is one of the most important regions of petroleum exploration. For example, Santos et al. (2006) investigated the electrochemical remediation of oil extraction industry wastewater using Ti/Ru_{0.34}Ti_{0.66}O₂ anode. The authors obtained the best COD reduction (57%) of an oily sample for 70 h at 50 °C with a current density of 100 mA cm⁻², but the slow rate of COD reduction could be attributed to the occurrence of secondary reactions involving O₂, Cl₂ and H₂ evolution. Also, 24%, 48% and 57% COD reduction after 70 h of electrolysis at 10 °C, 25 °C and 50 °C were achieved, respectively.

Zanbotto Ramalho et al. (2010) studied the anodic oxidation of organic pollutants from PW generated by petroleum exploration of the Petrobras plant-Brazil using an electrochemical reactor with a Ti/RuO₂-TiO₂-SnO₂ electrode. Under galvanostatic conditions ($j = 89 \text{ mA cm}^{-2}$), it was found that the organic pollutants degradation, using different flow rates (0.25, 0.5, 0.8 and 1.3 dm³/h), achieved distinct removal efficiencies (98%, 97%, 95% and 84% were achieved, respectively). Significantly, under the same conditions, electrochemical process achieved poor degradation of phenol and ethyl benzene: 20–47% (at 0.25, 0.8 and 1.3 dm³/h) and 17–47% (at 0.25, 0.5, 0.8 dm³/h), respectively. Figure 1 evidences the pollutants removal obtained by GC results obtained under above experimental conditions. Complete elimination of pollutants was obtained after 0.5–2.5 h of electrolysis, with energy consumption values ranging from 4.84 to 0.97 kWh m⁻³ and removal prices from 0.14 to 0.61 US\$ (from 0.11 to 0.5 Euros).

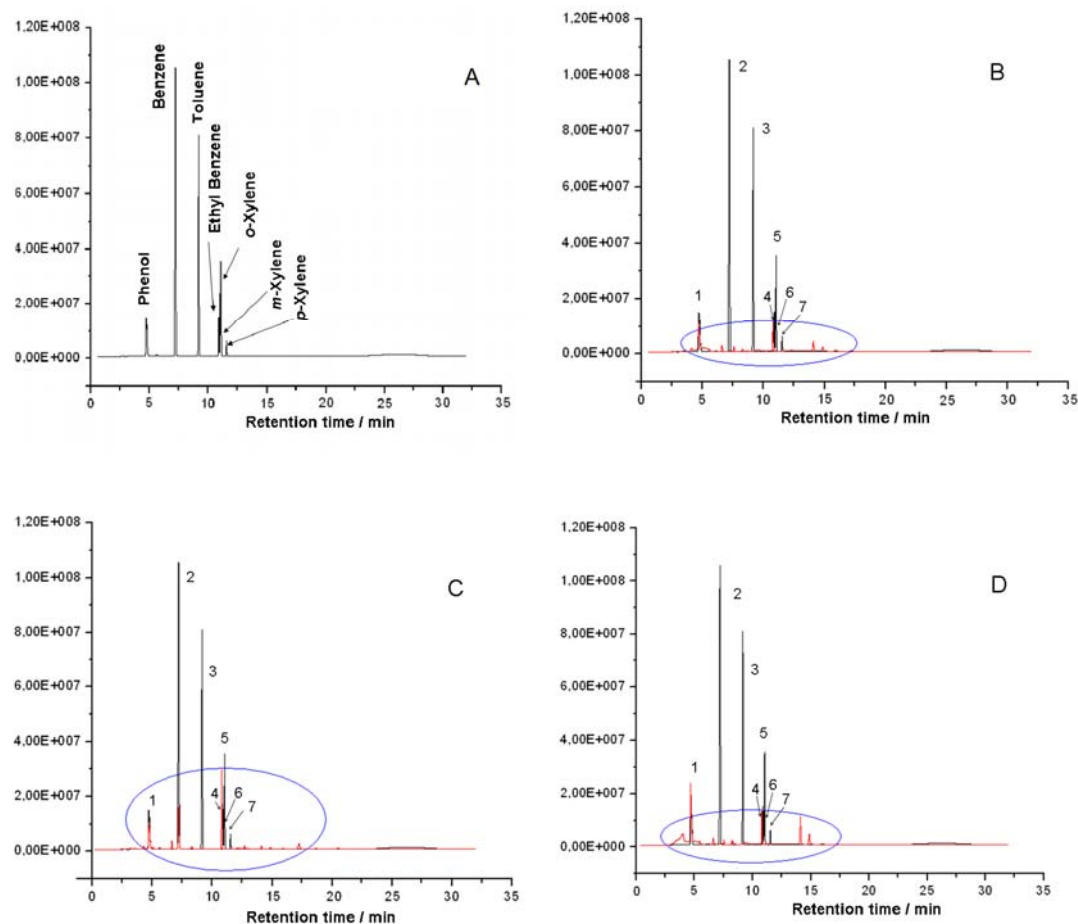


Figure 1. (A) Identification and quantification of the organic pollutants contained in PW samples, according to the chromatography conditions described in analysis section. Effect of flow rate on organic pollutants removal by controlled current density electrolysis (89 mA cm^{-2}). Experimental conditions: $T = 25 \text{ }^{\circ}\text{C}$; DSA electrode area 19 cm^2 , NaCl: 15000 g dm^{-3} , pH: 6.86, flow rate: (B) $0.5 \text{ dm}^3/\text{h}$, (C) $0.8 \text{ dm}^3/\text{h}$ and (D) $1.3 \text{ dm}^3/\text{h}$. Symbols: 1) Phenol; 2) Benzene; 3) Toluene; 4) Ethyl benzene; 5) o-Xylene; 6) m-Xylene and 7) p-Xylene. PW samples contain approximately $20\text{--}30 \text{ mg dm}^{-3}$ of benzene, toluene, ethyl benzene, xylenes, and 5 mg dm^{-3} of phenol.

Bezerra Rocha et al. (2012) investigated the anodic oxidation of real PW, generated by petroleum exploration of the Petrobras plant from Brazil, using platinum supported on Ti (Ti/Pt) and boron-doped diamond (BDD) anodes in an electrolytic batch cell. The influence of several operating parameters such as current, supporting electrolyte, agitation rate and temperature on the performance was studied and the

energy consumption was also evaluated. Results clearly showed that BDD promotes complete COD removal (98%) due to the high amounts of effective hydroxyl radicals and peroxodisulfates generated from water oxidation. COD removal rate increased notoriously when an increase on the current density (from 15 to 60 mA cm⁻²) was applied. Conversely, at Pt electrode, about 50% of COD removals were achieved by applying 15 and 30 mA cm⁻² of current density, and 80% of COD removal at 60 mA cm⁻². When GC-MS analysis was performed to determine the concentration of the principal petroleum hydrocarbons eliminated; a comparison between the elimination of these organic pollutants as a function of applied current densities (15 and 30 mA cm⁻²) and experimental conditions (real discharged conditions, Na₂SO₄ dissolved in the effluent and temperature) demonstrated that more than 95% of the organic compounds were completely oxidized as well as heavy metals were removed. However, higher energy consumption and longer process time were accomplished, limiting the applicability of this technology for complete treatment of petrochemical wastewaters.

On the other hand, a study has evaluated the efficiency of Ti/RuO₂ anode in degrading organic substances, present in wastewaters from petroleum industry, before their discharge or reuse using an electrochemical flow reactor with higher anode area (Santos et al., 2013). The COD removals, after 120 min of electrolysis, with a current density of 10 mA cm⁻², anodic area of 107 cm², flow rate of 0.54 mL s⁻¹ and at 25°C, were above 96%, for effluent after flotation, with 712 mg L⁻¹ COD, and 87% for effluent before flotation, with 833 mg L⁻¹ COD. Partial COD removal from both effluents was achieved when current density was increased from 10 to 30 mA cm⁻². The increase of current density also favoured a decrease of the electrolysis time necessary to achieve a complete COD removal from both effluents. However, current density increase also led to higher specific energy consumption. For example, for the effluent before flotation treatment, the cost of the energy necessary to achieve a complete COD removal in 60 min was around 38 US\$ kgCOD⁻¹ (28.5 Euros kgCOD⁻¹), while that for effluent after flotation treatment, under similar conditions after 30 min of electrolysis was only 28 US\$ kgCOD⁻¹ (21 Euros kgCOD⁻¹). Results showed that Ti/RuO₂ electrode can be an efficient alternative for the treatment of effluents containing residues of petroleum and petroleum products.

Recently, the scale-up of electrochemical flow system was investigated by treating petrochemical wastewater using Ti/Pt and BDD anodes by Dos Santos et al. (2014). An electrochemical flow cell was used in order to find the best condition for the anodic treatment of the petrochemical wastewater (employing the PW samples as received from petrochemical industry). Preliminary experiments were performed at 25°C for studying the role of anode material (Ti/Pt and BDD anodes with 63.5 cm²) and applied current density ($j=20, 40$ and 60 mAcm⁻²). Results clearly indicated that higher COD removals were achieved at different applied current densities, using Ti/Pt and BDD anodes (see, Fig. 2). At 20, 40 and 60 mAcm⁻² using Ti/Pt electrode, 64.5% 90.7% and 93.6% of COD removals were achieved, respectively. Under similar conditions, at BDD anode, 76.2%, 94.5% and 97.1% of COD elimination were obtained in 8 h of treatment. Total current efficiencies were estimated by applying 20, 40 and 60 mAcm⁻², for Pt anode, achieving 58%, 41% and 29%; whereas at BDD anode, 70%, 54% and 39% were attained, respectively. These values confirm that an amount of current is employed in oxygen evolution reaction (undesired reaction) after the first hours of treatment, decreasing the total efficiency of electrochemical oxidation reaction. The effect of temperature during the electrochemical treatment of petrochemical effluent (employing the PW samples as received) was also studied by applying 40 mA cm⁻², varying the temperature (25, 40 and 60°C). These temperatures were selected; because these mimic the real temperatures of the petroleum platform discharges. It was observed that changes in temperature have a strong influence on oxidation rate by applying 40 mA cm⁻² at Ti/Pt anode, reducing treatment times. COD removals after 5 h of treatment were of 83.2%, 87.4% and 92.1% at Ti/Pt; while for BDD the influence on temperature contributes with a modest increase on oxidation rate, COD removals of 81.9%, 91.8% and 94.5% were achieved. It is important to remark that, under high concentrations of NaCl in solution (a key characteristic of petrochemical effluents) EO via ·OH radicals is not the only oxidation mechanism that occurs on electrochemical treatment. In this case, chlorohydroxyl radicals are also generated on anode surface, and consequently oxidizing organic matter. Therefore, Silva et al. (2013) studied the anodic oxidation of three classes of produced water (PW) (fresh, brine and saline) generated by petrochemical industry using Ti/IrO₂-Ta₂O₅ and BDD electrodes in a flow reactor. Different types of PW found in oilfields: fresh, brine and saline, which are assigned to the direct influence of the characteristics of the soil where they are confined. During electrochemical treatment, various operating parameters were investigated, such as temperature, pH, conductivity, current density, total organic carbon (TOC), chemical oxygen demand (COD) as well as energy consumption and cost. The use of these electrode materials was proposed by them because the electrocatalytic features to produce in-situ strong oxidant species, principally active chlorine, is a key point that must be investigated to propose the applicability of this method as a pre-treatment process for the petrochemical industry. To understand the performance of the electrochemical

treatment, mainly due to different concentrations of chloride ions, different applied current densities were used for each type of PW (fresh, brine and saline), evaluating the efficiency of the anode materials (Ti/IrO₂-Ta₂O₅ and BDD) (Silva et al., 2013). In the case of fresh PW, results clearly demonstrated that when lower current densities were applied, lower Q was employed, avoiding a complete elimination of COD, principally when Ti/IrO₂-Ta₂O₅ was used as electrocatalytic material. Conversely, when BDD anode was employed, lower Q was necessary to achieve a significant COD removal by applying 2.5 and 5 mA cm⁻². Higher TOC removal efficiencies were achieved on BDD (ranging from 40% to 90%) respect to the %TOC removals obtained at Ti/IrO₂-Ta₂O₅.

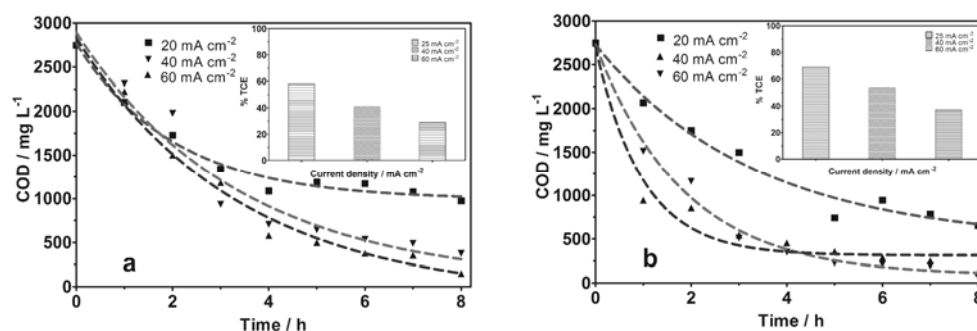


Figure 2. Influence of applied current density on the COD removal as a function of time and total current efficiency (inset) during PW anodic oxidation using (a) Ti/Pt and (b) BDD anodes. Operating conditions: PW sample, as obtained from Brazilian platform, applied current density = 20, 40 and 60 mA cm⁻², Temperature=25 °C, flow rate: 151 L h⁻¹.

For brine PW, results showed that the COD decay, at different applied current density (10, 20, and 30 mA cm⁻²) for Ti/IrO₂-Ta₂O₅ and BDD anodes, depends on applied current density as well as the Q. Complete COD removal was achieved by applying 30 mA cm⁻² at Ti/IrO₂-Ta₂O₅, after approximately 240 min of electrolysis ($\approx 6 \text{ Ah dm}^{-3}$), while at 10 and 20 mA cm⁻², a partial COD removal was achieved, about 71.5% (2 Ah dm⁻³) and 78.6% (4.2 Ah dm⁻³), respectively. However, TOC results indicated that the effluent seems to have some recalcitrant compounds (or degradation products) that are not oxidized under these experimental conditions. For BDD anode, under the same experimental conditions, complete COD removal was achieved at all current densities (after 1.7 Ah dm⁻³ (10 mA cm⁻²), 3 Ah dm⁻³ (20 mA cm⁻²) and 4 Ah dm⁻³ (30 mA cm⁻²)), decreasing remarkably the electrolysis time. Considering that, the effluent had higher concentrations of Cl⁻ in solution; it promoted the production of active chlorine species and consequently, favouring a faster COD abatement. Also, TOC removals ranged from 92 to 99%, indicating that the degradation process occurs with no significant formation of recalcitrant intermediates.

During the electrochemical treatment of saline PW using Ti/IrO₂-Ta₂O₅ and BDD electrodes at 25 °C was observed that at both materials, COD decay was slight after 8 h of electrochemical treatment, independent on applied current density (10 mA cm⁻² or 20 mA cm⁻²). Results clearly showed that a modest anodic oxidation of saline PW was performed, achieving 50% of COD removal by applying 10 and 20 mA cm⁻², at Ti/IrO₂-Ta₂O₅ electrode after 3.5 and 7 Ah dm⁻³, respectively. The mineralization rate (TOC removal (37%)) was not significantly influenced by the higher concentrations of chloride in the petrochemical effluent, suggesting that the production of Cl₂ is the preferential reaction. Likewise, for BDD anode, the COD removal, under similar conditions, occurs with similar efficiencies than those achieved for Ti/IrO₂-Ta₂O₅. On the other hand, 44% of COD removal was achieved for BDD independent on applied current density due to two features: higher Cl⁻ concentrations (86875 mg dm⁻³) and higher initial COD (11541 mg dm⁻³). The degradation process when higher Cl⁻ concentrations are present in the effluent, it occurs with significant formation of Cl₂ gas in concomitance with higher production of O₂, complicating the complete oxidation of organic matter. Also, higher initial COD is traduced in the production of several by-products decreasing the efficiency process and this assertion was in agreement with the TOC efficiencies obtained during electrochemical treatment of saline PW by applying 10 and 20 mA cm⁻² of current density (Silva et al., 2013).

Recently, an important study was published by Gargouri e co-workers (Gargouri et al., 2014) where the anodic oxidation of real PW, generated by the petroleum exploration of the Petrobras plant-Tunisia was investigated using Ta/PbO₂ and BDD anodes were used as anodes by 30, 50 and 100 mA cm⁻² in an electrolytic batch cell. The electrolytic process was monitored by the COD and the residual total petroleum hydrocarbon (TPH) in order to know the feasibility of electrochemical treatment. The COD removal was approximately 85% and 96% using PbO₂ and BDD reached after 11 and 7 h, respectively. Compared with PbO₂, the BDD anode showed a better performance to remove petroleum hydrocarbons compounds from PW. It provided a higher oxidation rate and it consumed lower energy. The average energy consumption values at the end of electrochemical treatment were 38 and 46 kW h m⁻³ by using BDD and PbO₂ electrodes, respectively. As it can be observed, BDD consumed less energy than PbO₂ anode but achieved higher COD removal than PbO₂. For example, to reach 85% of the COD removal, BDD and PbO₂ consumed 24 and 46.2 kW h m⁻³, respectively. Cytotoxicity evaluations shown that electrochemical oxidation using BDD could be efficiently used to reduce more than 90% of hydrocarbons compounds.

3. Concluding remarks

The results of our investigations demonstrated that anodic oxidation can be used successfully to remove completely organic pollutants from petrochemical wastewaters. In the case of petrochemical effluents, the efficiency decontamination and time process depend on the operating conditions, such as current density, electrolyte, temperature and nature of material. Although the electrical dependence and process time could make useless the electrochemical approach for complete treatment of petrochemical wastewaters; it can be a feasible process as a pre-treatment process reducing significantly the cost and time treatment. Electrochemical oxidation system could be scaled up as large as required without performance deterioration by increasing the total anode area and modifying the hydrodynamic configuration of cell.

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