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Electrochemical treatment of fresh, brine and saline produced water generated by petrochemical industry using Ti/IrO_2–Ta_2O_5 and BDD in flow reactor

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HIGHLIGHTS

- Electro-oxidation using DSA® and BDD removes efficiently the dissolved organic matter from PW.
- BDD electrode shows better performance for removal COD.
- DSA® electrode operates with lower energy consumption and operating cost.
- The dominant process on DSA® and BDD electrodes is indirect oxidation.
- Cl^- favors the indirect electro-oxidation by formation of chlorine/hypochlorite.

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ABSTRACT

This study compares the anodic oxidation of three classes of produced water (PW) (fresh, brine and saline) generated by petrochemical industry using Ti/IrO_2–Ta_2O_5 and BDD electrodes in a flow reactor. 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. When both electrodes materials are compared under the same operating conditions, higher TOC and COD removal efficiencies were achieved for BDD anode, nevertheless, the energy consumption and cost were higher when compared with the values estimated for Ti/IrO_2–Ta_2O_5. Different Cl^- concentrations in the effluents promoted the electrogeneration of strong oxidant species, such as chlorine and hypochlorite, increasing the efficiency of treatment. These results encourage the applicability of this method as a pre-treatment process for the petrochemical industry, reducing depuration time.

1. Introduction

The petrochemical companies deal with problems of difficult solution in relation to activities aimed at environmental protection, due to the generation of large amounts of waste during oil prospecting and exploitation, such as produced water (PW). The amount of this kind of waste varies depending on the oil reservoir: a new basin produces 5–15 vol.%, while at the end of its lifetime it reaches 75–90 vol.% [1].

PW contains with different pollutants, such as heavy metals (Cd, Cr, Cu, Pb, Hg, Ag, Ni, Zn), organic compounds, and dissolved/suspended solids. Benzene, toluene, xylene, phenol, halogenated aromatic compounds, chloroform and trichloroethylene are the major organic pollutants present in PW, commonly known as BTEX [1]. Also, the composition of PW depends on chloride concentration, determining if it is fresh, brine or saline PW.

Due to their toxicity and their potential carcinogenic effect, these effluents can cause irreparable damage to human health and the environment [2–5]. Several alternative treatment of PW has been studied by several research groups around the world [2]. The physical–chemical and bioremediation methods utilized for the degradation of these compounds have shown various operational problems, such as: generation of toxic gases, phase transfer of pollutants, residual sludge production, demand for large territorial areas and the impossibility of destroying refractory compounds [6].

In the last years, the electrochemical technology has been proposed as an alternative process for elimination of contaminants in effluents, showing excellent results in various matrices such as

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textile dyes [7–13], dairy [14,15], herbicides/pesticides [16–20], heavy metals [21], aquaculture [22], landfill leachate [23], pharmaceutical residues [24–28], pulp and paper [29], among others. Moreover, a wide variety of electrode materials have been suggested, such as dimensionally stable anodes, noble metals (e.g. platinum), carbon-based anodes, PbO_2 and BDD; obtaining different removal organic matter efficiencies [30–33] considering that non-active anodes, such as BDD, are useful for direct oxidation of organic material via hydroxyl radicals, while DSA, such as Ti/IrO_2–Ta_2O_5, are effective for promoting hypochlorite mediated chemistry when chloride is present.

In the case of applicability of electrochemical technology for treating petrochemical wastewaters, dimensionally stable anodes, platinum and BDD have been preferentially used as electrocatalytic materials [34]. However, in some cases, Pt anodes are very expensive, and also subject to fouling. Recently, Santos et al. [35] investigated the electrochemical remediation of oil extraction industry wastewater using Ti/$Ru_{0.34}Ti_{0.66}O_2$ 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 [35], but the slow rate of COD reduction was attributed to the occurrence of secondary reactions involving O_2, Cl_2 and H_2 evolution. Also, 24%, 48% and 57% COD reduction after 70 h of electrolysis at 10 °C, 25 °C and 50 °C were achieved, respectively. On the other hand, using Pt/Ir electrodes, the electrochemical purification of bilge water (COD_0 = 3080 mg dm^{-3}, 50/50% seawater/fresh water composition) were investigated by Körbahti and Artut [36], where COD removals ranging from 85–100% were achieved by applying 12.8 mA cm^{-2} of current density at 32 °C.

The anodic oxidation of PW generated by petroleum exploration of the Petrobras plant–Brazil using an electrochemical reactor with a Ti/RuO_2–TiO_2–SnO_2 was recently studied [3]. Under galvanostatic conditions (j = 89 mA cm^{-2}), it was found that the organic pollutants degradation using different flow rates (0.25, 0.5, 0.8 and 1.3 dm^{-3} h) achieved distinct removal efficiencies (98%, 97%, 95% and 84% were achieved, respectively).

More recently, Rocha et al. [5] studied the electrochemical oxidation of brine PW in galvanostatic conditions using platinum supported on titanium (Ti/Pt) and BDD anodes, employing a batch reactor. The results showed that complete COD removal was achieved using BDD electrode due to the production of high amounts of hydroxyl radicals (·OH) and oxidizing species (Cl_2, HClO, ClO^-).

The use of these electrode materials have been proposed due to electrocatalytic features to produce *in situ*-strong oxidant species, principally active chlorine. However, studies reported in literature relative to the treatment of petrochemical effluents, especially PW, have not contemplated the 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. Therefore, the objective of this study was to evaluate the performance of Ti/IrO_2–Ta_2O_5 and BDD electrodes during treatment of real PW (fresh, brine and saline) using an electrolytic cell in continuous flow, focusing our attention on the electrochemical conditions that provide greater efficiency of current with lower power requirement to scale up the electrochemical treatment in order to employ in petrochemical platforms.

2. Experimental

2.1. Produced water samples and chemicals

The PW samples (fresh, brine and saline) were supplied by Petrobras Plant in Rio Grande do Norte, northeastern region of Brazil. The characteristics of the effluents samples were analyzed using American Public Health Association (APHA) procedures [37] and given in Table 1. Chemicals were of the highest quality commercially available, and were used without further purification. The classification of PW, as fresh, brine and saline, was performed according to the salinity of the samples (see Table 1).

Table 1
Results of physical and chemical analyzes of PW samples.

Analytical parameters	PW fresh	PW brine	PW saline
Temperature (°C)	40.2	42.0	40.1
pH	6.87	7.83	7.03
Conductivity (mS cm^{-1})	0.61	5.16	143.9
COD (mg dm^{-3})	250	700	11,541
Salinity (mg dm^{-3})	78.8	2593	143170
Chloride (mg dm^{-3})	47.8	1573	86,875
TOC (mg dm^{-3})	458	1186	15,015
Benzene (μg dm^{-3})	6.45	5.45	4.35
Toluene (μg dm^{-3})	5.48	7.02	6.89
Ethylbenzene (μg dm^{-3})	28.2	37.2	7.20
o-Xylene (μg dm^{-3})	5.81	4.86	5.86

Limits permitted by Brazilian legislation (mg dm^{-3}): benzene = 1.2; toluene = 1.2; ethylbenzene = 0.84 and xylene = 1.6.

2.2. Instrumentation

The analysis of pH, conductivity and temperature were performed using a multiparameter instrument – model 5 Star Orion (USA). The analysis of COD were performed using a multiphotometer HANNA – model HI 83,099 (Brazil), after digestion of samples in a Term Reactor HANNA – model HI 839,800 (Brazil); and the electrolysis were carried out using a power supply MINIPA MLP-3303 (Brazil). COD reflects the amount of organic matter (biodegradable and refractory) removed during process [38] and the COD decay was used to evaluate the performance of the electrooxidation experiments. It is important to remark that, chloride is an interference of COD method; however, the Cl^- limit for obtaining accurate results using commercially available digestion vials is 2000 mg dm^{-3}, allowing the COD determinations for fresh and brine PW effluents. In the case of saline PW, precipitation of Cl^- before COD determination was performed; allowing to obtain accurate data. Total organic carbon (TOC) content is also an indicator of environmental pollution and it is important for environmental control of water and wastewater. TOC analyzer used in the present study was Analytik Jena Multi N/C 3100 (Germany).

2.3. Electrolytic systems

The electrochemical oxidation was conducted in galvanostatic conditions using an electrolytic flow cell [11]. PW effluent was stored in a reservoir of 1.5 dm^3 and it was recirculated through the electrolytic cell by means of a centrifugal pump, working in the flow of 160 dm^3 h^{-1}. The cell contained a Ti/IrO_2–Ta_2O_5, Ti/PbO_2 or BDD electrode as anode and a Ti plate as cathode. The electrodes were circular and each of them had a geometric area of 63.5 cm^2, and with a separation of 1.0 cm between them. Ti/IrO_2–Ta_2O_5 electrode was supplied by Industrie De Nora Elettrodi (Milan, Italy). BDD electrode was supplied by Adamant Technologies with doping level of boron in the diamond layer of 1000 ppm. Electrochemical oxidation experiments were maintained at 25 °C, to assess the role of applied current density to investigate the treatment of fresh PW (1, 2.5 and 5 mA cm^{-2}); brine PW (10, 20 and 30 mA cm^{-2}) and saline PW (10 and 20 mA cm^{-2}). Furthermore, the temperature effect was investigated by carrying out experiments at 40 °C and applying a current density of 5 and 20 mA cm^{-2} to fresh and brine PWs, respectively; the temperature of the effluents was controlled using a thermostatic bath. The cell