



## Fuel station effluent treatment by electrochemical technology



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### ABSTRACT

In this work, a real effluent from oil–water separator of fuel station has been treated for the first time by electrochemical oxidation (EO) process. Electrochemical experiments were carried out under real discharged effluent conditions using Ti/Pt and Ti/IrO<sub>2</sub>–Ta<sub>2</sub>O<sub>5</sub> anodes at different supporting electrolytes in order to study the influence of the different oxidants electrogenerated. The effect of applied current densities ( $j = 10, 20$  and  $30 \text{ mA cm}^{-2}$ ) was also evaluated. Results showed that good performances were achieved using Ti/Pt anode adding K<sub>2</sub>SO<sub>4</sub> as supporting electrolyte to improve the solution conductivity. Dissolved organic carbon (DOC) and chemical oxygen demand (COD) abatements of 55.2% and 61.5% were achieved, reducing significant concentration of organic compounds (in terms of benzene–toluene–ethylbenzene–xylene (BTEX) and total petroleum hydrocarbons (TPHs)) at  $j = 30 \text{ mA cm}^{-2}$  after only 4 h of electrochemical treatment. Affordable costs of process expenditure of US\$ 3.79 m<sup>-3</sup> were also achieved using Ti/Pt anodes; however, these costs could be reduced increasing the solution conductivity. The figures obtained in this investigation provide valuable information for developing of electrochemical technologies to their real application in order to propose a pre or post treatment alternative.

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### 1. Introduction

Petroleum companies generate high amounts of wastewater effluents containing oil and other petrochemical residues from the oil refineries, petrochemical industries, natural gas processing plants, fuel stations and other activities [1]. In the case of fuel dispensers, these are used to pump petrol/gasoline, diesel, ethanol fuel, biofuels like biodiesel, kerosene, or other types of fuel into the tanks within vehicles [2,3]. Generally, the area around the fuel dispensers must have a drainage system [2] because sometimes the fuel spills on the ground, and it can be transported by any liquids (rainwater, washing fluids, etc.) and consequently, it penetrates in the soil or contaminate groundwater [4]. For this reason, water polluted with fuel enters in a petrol interceptor (oil–water separators) before to a discharge of effluent in the sewer.

Oil–water separators are devices that have been designed to separate and recover gross amounts of oil and suspended solids from oil wastewaters [4,5]. However, after this revalorization process, noxious persistent organic pollutants are still present in low concentration and remaining oil that has not been properly separated. This oil is formed by a mixture of hydrocarbons which are quantified as total petroleum hydrocarbon (TPH), because the quantification of each hydrocarbon

separately is not practical. TPH quantification shows the sum of volatile petroleum hydrocarbons (from C<sub>2</sub> up to C<sub>5</sub>) and extractable petroleum hydrocarbons (from C<sub>6</sub> up to C<sub>40</sub>). These compounds are highly recalcitrant and affect the environment as well as the animal and human health [6,7]. Nevertheless, the derivative aromatic compounds are the most harmful and hazardous pollutants in the TPH mixture. Among the aromatic pollutants found in oil–water separators wastewater effluents, the most important mixture is related to benzene, toluene, ethylbenzene and xylenes, commonly identified by the acronym BTEX. The low concentration of compounds of BTEX in water difficult their removal by conventional wastewater treatments and these persist largely in the aquatic environment, then being dangerous due to their toxicity and their carcinogenic properties [8,9].

Few studies have reported the elimination of BTEX from water by adsorption [10], chemical oxidation [11] and bioreactors [12]. However, these methodologies require long treatment times (up to days) or generate other residues [13]. Consequently, the application of other advanced technologies has been encouraged. In this context, EAOPs are emerging methods developed as eco-friendly and efficient alternative to mineralize low contents of persistent organic pollutants in waters [13–15]. EAOPs are based on the in situ electrogeneration of reactive oxygen species (ROS) and other oxidant species such as active chlorine species. The simplest and most popular EAOP is EO where organic pollutants in solution are oxidized by direct charge transfer at the anode (M), or extensively destroyed by physisorbed hydroxyl radical (M(•OH)) produced as intermediate from water oxidation on

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anode materials with high over-potential of  $O_2$  evolution from reaction (1) [15,16]. This radical has a very high standard reduction potential ( $E^\circ(\bullet OH/H_2O) = 2.80$  V/SHE) that can react with most organics up to complete combustion.



The production of hydroxyl radicals depends strongly on the nature of anode material used. Boron-doped diamond anodes generate greater amounts of reactive  $M(\bullet OH)$  than other anodic materials for EO [16–18]. However, the material acquisition cost and their higher energy consumption incentivize the use of alternative cheaper materials besides present lower operational costs, such as Ti/Pt and mixed metal oxide electrodes such as  $IrO_2$ ,  $RuO_2$ ,  $SnO_2$  or their mixtures. In the case of mixed oxide anodes, also called as dimensional stable anodes (DSA), present low oxidation power [19–22] than boron-doped diamond, favoring preferentially electrochemical conversion. However, DSA anodes are more effective for wastewater treatment when the electrogeneration of several oxidant species is promoted, such as active chlorine species, persulfate, and ozone [22–24]. In the case of active chlorine species, the interest in this oxidant is based on the ubiquitous presence of chloride ions in a certain number of effluents and natural waters, making possible the electrogeneration of this highly oxidant species during the electrochemical treatment due to the oxidation of  $Cl^-$  [13] that yields  $Cl_2(aq)$  from reaction (2). When this electrogenerated chlorine diffuses away from the anode, it is hydrolyzed to be disproportionated to HClO and  $Cl^-$  ion (reaction (3)). Further, HClO presents an acid–base equilibrium with  $ClO^-$  ion with  $pK_a = 7.55$  by reaction (4).



The increase in current may accelerate reaction (2) also enhancing the production of these active chlorine species which are able to oxidize more rapidly the organic matter in competition with  $M(\bullet OH)$  [25].

The use of EAOPs by direct or indirect approaches has shown promising results on the complete abatement of POPs in synthetic and real effluents such dyes [20,26–28], drugs [29–31], pesticides [32–34], petrochemical wastes [35–41] and tannery wastewaters [42]. In contrast, no attempts have been published about the use of electrochemical technologies for decontamination of polluted effluents generated by fuel stations. More attention has been focused on the treatment of this kind of liquid wastes by other methods (flotation, coagulation, biological treatment, membrane separation technology, combined technology and advanced oxidation process) [2,43,44]; for this reason, to gain a better understanding on the efficiency and applicability of EAOPs, we investigated their viability to remove efficiently BTEX and TPH from effluents of oil–water separators of a fuel station by EO using a electrochemical cell with Ti/Pt and  $Ti/IrO_2-Ta_2O_5$  electrodes. To do this, the role of the generated oxidizing agents was clarified from the effect of the applied  $j$  and the supporting electrolyte used on the performance of each one of the electrocatalytic materials tested. The abatement of organic matter was also measured in terms of chemical oxygen demand (COD) removal and dissolved organic carbon (DOC) values as well as the determination of TPH and BTEX concentrations were performed at the end of electrochemical treatment to evaluate the efficacy of EO to treat this kind of effluent.

## 2. Experimental

### 2.1. Oil–water separator effluent characteristics

The effluent sample was collected from an oil–water separator at a fuel station situated in the metropolitan region of Natal (Northeast

Brazil). A water sample of 40 L was collected after the phase separation process and used for all the experiments carried out at lab-scale. It is worth noting that the physical–chemical characteristics resumed on Table 1 were determined from an actual effluent of an operating oil–water separator.

### 2.2. Chemicals

Anhydrous potassium sulfate and sodium chloride were of analytical grade supplied by Ventech. Benzene, toluene, ethylbenzene, o-xylene, m-xylene and p-xylene used as pattern compounds to quantify the BTEX by gas chromatography were of analytical grade ( $\geq 99\%$ ) by Sigma-Aldrich. Other chemicals and solvents were of HPLC grade purchased from Fluka.

### 2.3. Electrolytic systems

A scheme of the 2 L recirculation flow electrochemical system used to perform the EO treatment is shown in Fig. 1. The effluent collected was introduced into the reservoir and recirculated through the system using a pump at a flow rate of  $310$  L  $h^{-1}$  regulated with a flowmeter. The solution passed through an undivided reactor with  $63.5$  cm<sup>2</sup> electrodes of electroactive area with an interelectrode gap of  $1.3$  cm, returning after that to the reservoir. The electrochemical cell contained either a Ti/Pt or  $Ti/IrO_2-Ta_2O_5$  anodes from DeNora Electrodes (Italy) while the cathode was a Ti plate. Electrolyses were performed galvanostatically using a DC-MPL 3305 M power supply at different applied current densities of  $10$ ,  $20$  and  $30$  mA  $cm^{-2}$ . Before the electrochemical treatment  $1.5$  g  $L^{-1}$   $K_2SO_4$  or  $1.5$  g  $L^{-1}$  NaCl was added (these concentrations were chosen based on the existing literature [13,15,20, 22–24]) as electrolyte to improve the effluent conductivity and to study the influence of the supporting electrolyte on the electrochemical degradation of TPH and BTEX.

### 2.4. Apparatus and analytical procedures

The solution pH was measured on a Tecnal pH-meter. Reproducible dissolved organic carbon (DOC) values with an accuracy of  $\pm 1\%$  were obtained using an Analytik Jena Multi NC 3100 total organic carbon analyzer. Chemical oxygen demand (COD) concentrations were determined using the HANNA COD tube tests (range  $0$ – $1500$  mg  $L^{-1}$ ) and a HANNA photometer COD-HI 83,099, after digestion procedure. From COD values the overall efficiency has been evaluated from the Instantaneous Current Efficiency (ICE, in.%) values for EO estimated from Eq. (5) [13,15]:

$$\%ICE = FV \frac{(COD_0 - COD_t)}{8I\Delta t} \times 100 \quad (5)$$

**Table 1**  
Water effluent characteristics.

Parameters	Values
DOC (mg C $L^{-1}$ )	$788.7 \pm 0.5$
COD (mg $O_2$ $L^{-1}$ )	$901 \pm 2$
TOG (mg $L^{-1}$ )	$70 \pm 1$
pH	$6.9 \pm 0.2$
Turbidity	$5.8 \pm 0.5$
Benzene ( $\mu g$ $L^{-1}$ )	$311.2 \pm 0.5$
Toluene ( $\mu g$ $L^{-1}$ )	$1228.5 \pm 0.5$
Ethylbenzene ( $\mu g$ $L^{-1}$ )	$136.7 \pm 0.5$
Xylene ( $\mu g$ $L^{-1}$ )	$318.9 \pm 0.5$
BTEX ( $\mu g$ $L^{-1}$ )	$1995.4 \pm 0.5$
TPH (mg $L^{-1}$ )	$844.6 \pm 0.5$

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