Research Article

Electrochemical Incineration of Phenolic Compounds from the Hydrocarbon Industry Using Boron-Doped Diamond Electrodes

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Electrochemical incineration using boron-doped diamond electrodes was applied to samples obtained from a refinery and compared to the photo-electro-Fenton process in order to selectively eliminate the phenol and phenolic compounds from a complex matrix. Due to the complex chemical composition of the sample, a pretreatment to the sample in order to isolate the phenolic compounds was applied. The effects of the pretreatment and of pH on the degradation of the phenolic compounds were evaluated. The results indicate that the use of a boron-doped diamond electrode in an electrochemical incineration process mineralizes 99.5% of the phenolic sample content. Working in acidic medium (pH = 1), and applying 2 A at 298 K under constant stirring for 2 hours, also results in the incineration of the reaction intermediates reflected by 97% removal of TOC. In contrast, the photo-electro-Fenton process results in 99.9% oxidation of phenolic compounds with only a 25.69% removal of TOC.

1. Introduction

Residual discharges from refineries are complex matrices of varied chemical composition. Among the most dangerous organic contaminants, phenol stands out as a highly toxic compound, which is also biorefractory [1–8]. A typical phenol concentration in industrial discharges from refineries oscillates within a range of $20-200 \text{ mg L}^{-1}$ [3, 8, 9], although the actual concentration value can vary depending on the nature of the process [8]. A concentration in the range of $5-25 \text{ mg L}^{-1}$ is as toxic for aquatic life as it is for humans [1, 2] and in response to this situation, the maximum permitted limits of phenol residues found in industrial discharges vary between 0.5 and 1.0 mg L^{-1} [2]. In the case of potable drinking water, the European Union (EU), in its 80/778/EC directive, assigned a maximum permitted limit of $<0.0005 \text{ mg L}^{-1}$ for phenol in all of its forms [1], given that the consumption of water containing these compounds can induce cancer or death [10]. The elevated danger of this contaminant for aquatic life has marked phenol and some

phenolic compounds as priority contaminants, in agreement with the criteria of the Environmental Protection Agency (EPA) of the United States [1, 2].

The methods used in the treatment of wastewater for the elimination of phenol are separated into destructive [5, 10, 11] and nondestructive methods [1–4, 6, 12]. Among the destructive methods, biological processes are commonly used; however, no phenol degradation is observed at concentrations above 200 mg L⁻¹, and the microorganisms are completely deactivated at concentrations larger than 3000 mg L⁻¹ [1]. Another disadvantage that is observed in some destructive methods is that the successful degradation of phenol results in the generation of subproducts that are harder to degrade [11]. Other processes with destructive character that have been largely studied are the Fenton processes (Fenton, photo-Fenton, electro-Fenton, and photoelectro-Fenton) and the electrochemical oxidation technologies. Considering the last approach, the efficiency of the electrochemical reaction depends highly on the identity of the anode, which can significantly influence the reaction mechanism [8, 13]. It has been demonstrated that electrochemical oxidation with electrodes of high overpotential for oxygen such as Ti/PbO₂, Ti/SnO₂-Sb, and Ti/BDD allows, with high current efficiency, the complete elimination of organic contaminants as well as their intermediate products. On the other hand, the application of the Fenton processes in the treatment of refinery water residues has also been evaluated [8]. Although these processes permit the degradation of the contaminant, the degradation of the intermediates is not particularly feasible [8]. Recently, electrochemical oxidation using borondoped diamond (BDD) has won widespread acceptance due to the generation of hydroxyl radicals at high potentials, which are promoted in the interfacial zone through the water oxidation process (1). This allows the efficient degradation of the contaminant and of the subproducts of the reaction to CO₂ and H₂O (2), a process known as electrochemical incineration [13–16]

$$H_2O \longrightarrow {}^{\bullet}OH + H^+ + e^-$$
 (1)

$$R + M(^{\bullet}OH) \longrightarrow M + mCO_2 + nH_2O + H^+ + e^- \qquad (2)$$

Although both technologies show high efficiency in studies with synthetic samples, few studies have been carried out on samples obtained from actual refineries, where the efficiency of the reaction might be reduced due to the complex chemical composition of the effluent. This was made evident by Yavuz and Koparal [7] who evaluated the electrochemical oxidation of phenol in a parallel plate reactor using a ruthenium mixed metal oxide electrode, obtaining phenol removal efficiencies of 99.7% and 94.5% in synthetic and actual samples, respectively. In terms of chemical oxygen demand (COD), values of 88.9% and 70.1% were obtained for synthetic and actual samples, respectively, showing the effects of the chemical composition of actual discharge effluents. In another study, the degradation of phenol with Ti/TiO₂-RuO₂-IrO₂ from refinery samples showed only 74.75% and 48% removal of COD and TOC, respectively, although high quantities of chloride ions were employed [9]. However, these results should not be surprising, considering the composition of the sample and the natural activity of the electrodes. On the other hand, the use of Ti/RuO₂-TiO₂-SnO₂ in the treatment of hydrocarbon industry discharges has recently been evaluated, but the removal efficiency under the evaluated conditions was very low, 20%-47% [17]. Recently a comparative analysis was reported between Ti/BDD and the electro-Fenton approach in actual samples from refineries, indicating that the electro-Fenton process showed a better degradation of phenol in comparison to BDD, although the better degradation of the reaction intermediates (in terms of COD) occurred using BDD [8].

Previous works have shown the complexity that involves the treatment of wastewater from an actual discharge. However, they have also shown that the electrochemical oxidation with BDD seems to be a superior method, ahead of other technologies, given its capacity to incinerate many organic compounds as well as their reaction intermediates. In this work, we evaluate the selective degradation of phenolic compounds in actual samples from a refinery. The objective was to evaluate and compare the efficiency of the degradation of phenolic compounds with boron-doped diamond and with the photoelectro-Fenton process, applying an adequate pretreatment of the sample that allows the selective degradation of these contaminants.

2. Experimental Details

2.1. Characterization and Pretreatment of the Samples Obtained from the Refinery for Selective Degradation of Phenolic Compounds. Four different samples were obtained from a refinery and stored at 4°C before analysis. The determination of pH was performed with a Corning 450 potentiometer that was equipped with a Pinnacle glass electrode.

To avoid any interference that could reflect the presence of other contaminants in the electrochemical degradation of phenolic compounds, 4.5 L of each sample obtained from the refinery were treated with 10% NaOH in order to completely isolate the phenolic compounds from the original matrix. In this process, the selective isolation of phenolic compounds is carried out by the chemical conversion of phenols to phenolates. During this process 2 phases were obtained, one high-density aqueous phase and another with low density. Both samples were then stirred and after dichloromethane extraction, analyzed by GC-MS to identify the main components and to verify the effectiveness of the pretreatment. This analysis was performed using an Agilent 6890 Gas Chromatographer coupled to a 5973 N Mass Spectrometer. A HP-5 MS column (dimensions 30 m \times 0.25 mm, $0.25 \mu \text{m}$) was used with a stationary phase of 5% phenyl-methyl-siloxane. The carrier gas was helium grade 5 (UAP). The injection of the sample was performed in split mode 5:1, with a flow of 0.7 mL min⁻¹. The temperature of the injector was 543K, with an initial oven temperature of 323K (that was maintained for 4 minutes) and a ramp rate of 282K per minute until reaching a stable temperature of 573K for 6 minutes, for a total time of 37.78 minutes. Quantitative analysis of phenolic compounds of the preprocessed samples was performed using the 4-aminoantipyrine method [18]. Using this technique, the detection of phenolic compounds is carried out in their total form.

2.2. Electrochemical Incineration Using Boron-Doped Diamond. After accomplishing the chemical conversion of phenols to phenolates (aqueous phase with high density), three representative samples were taken to a specific pH value for their evaluation in alkaline, neutral, and acid conditions using HCl (Aldrich, analytical grade). These samples were subjected to electrolysis under galvanostatic conditions in a one-compartment electrolytic cell, with a capacity of 100 mL. The anode was boron-doped diamond (6.2 cm^2) and the cathode was Ti (12.5 cm^2). The system was operated at room temperature, with continuous stirring using a magnetic bar. All the experiments were carried out twice in order to confirm reproducibility. The degradation of phenol was monitored using the 4-aminoantipyrine method [18], and the degradation of the intermediates was evaluated through the analysis of total organic carbon (TOC), using a Shimadzu piece of equipment (Model TOC-VCSN). The removal percentages of TOC and phenol were calculated according to (3), where C_i is the initial (mg L⁻¹) and C_f is the final concentration (mg L⁻¹) [19, 20]

% removal =
$$\frac{C_i - C_f}{C_i} \times 100.$$
 (3)

2.3. Electrolysis with A Photo-Electro-Fenton System. The electrochemical destruction of phenolic compounds with the photoelectro-Fenton system was performed using a carbon fiber + TiO₂ anode and a nonmodified carbon fiber as cathode. A current of 0.2 A was imposed to the system for 2 hours, which contained 800 mL of waste water (aqueous phase with high density). The pH was fixed at 3 (adjusted with H₂SO₄). The previously O₂ saturated solution (30 minutes) was radiated with UV ligth ($\lambda = 365$ nm) using a lamp with a power output of 0.71 μ w cm⁻². In order to promote the generation of the Fenton reagent, 0.05 M Fe(SO₄) was added to the system. The electrolysis was performed at room temperature (20°C), with continuous agitation using a magnetic stirrer [21, 22].

3. Results and Discussion

3.1. Characterization and Pretreatment of the Samples Obtained from the Refinery for Selective Degradation of Phenolic *Compounds.* The pH of the samples (without any treatment) was 14. This pH value is related to the nature of the process, given that phenol is commonly used to synthesize chemical products in basic solutions [5]. Therefore, it is expected that the discharge has an alkaline pH. In order to ensure complete conversion of phenolic compounds to sodium phenolates, we proceeded to treat the samples using 10% NaOH. The GC-MS analysis of the pretreated samples showed that in the low-density aqueous phase, the principal components (qualitative analysis) were of aliphatic types (4-methyldecane, undecane, nonane, tridecane, tetradecane, decane, dodecane, pentacosane, and tricosane). In this analysis, the presence of phenolic compounds was not identified. The absence of phenolic compounds in the low density aqueous phase showed the effectiveness of the pretreatment. This result was verified with the chromatographic analysis of the high-density aqueous phase, where the phenolic compounds (2,4-dimethyl-phenol, 2-methyl-phenol, ocresol, 3-methyl-phenol, m-cresol, 1-methyl-phenol, pcresol, 3,5-dimethyl-phenol, 3-ethyl-5-methyl-phenol, 4benzyl-pyridacine, dibenzothiophene, 4-methyl-phenol, 2,4,6-trimethyl-phenol, 3-metoxy (methyltio)-phenol, 1methyl-3-phenoxy-benzene) were found. These results were expected considering that the chemical conversion process of phenol to phenolate in strongly alkaline conditions begins at pH 10 and reaches a maximum efficiency at pH 12 [23].

3.2. Electrolysis Using Boron-Doped Diamond. Before performing the degradation experiments, a preliminary analysis using a synthetic solution with a phenol concentration of 311 mg L^{-1} was carried out in an alkaline solution, with the goal of identifying the current to be applied. The currents



FIGURE 1: Electro-oxidation of a synthetic solution containing 311 mg L^{-1} of phenol in acid solution (pH 1) after the application of different current densities, using BDD and Ti as anode and cathode, respectively. The results are shown as normalized values (left) and percentages of degradation (right).

evaluated were 0.5, 1.0, 1.5, 2.0, and 2.5 A, for a 2hour period, under constant stirring. It was observed that the middle point of the removal was reached at 2 A (j = $0.32 \,\mathrm{A}\,\mathrm{cm}^{-2}$), as shown in Figure 1. Since in aqueous solution phenols exist as phenolates (phenoxide anions) with the degree of the dissociation increasing with the pH (pH above 12), a pH adjustment to acidic conditions was performed in order to favor the inverse process. Considering that full protonation should take place in the range of pH 2-4 [23] and that the efficiency in the electrochemical oxidation of phenolic compounds and phenol is better in the 0-3 pH range [24, 25], three different values of pH (1, 7 y 14) were evaluated applying the current density selected with the synthetic sample experiments (2 A). The concentrations of phenolic compounds in each sample were 1411, 1976, and 5928 mg L^{-1} for the pH values of 1, 7, and 14, respectively. The effect of the pH on the degradation process at 60 minutes is shown in Figure 2. The results show that the best degradation occurred at pH 1, followed by pH 7 and pH 14. The percentages of degradation were 40, 14, and 12%, respectively. After 120 minutes at pH 1, the efficiency of removal was greater than that of pH 7, with an initial concentration of 1411 mg L⁻¹ and a final concentration of 6.5 mg L^{-1} , representing a removal percentage of 99.5%, in comparison to 61.9% at pH 7. These results agree with those reported in the literature, where the efficiency of degradation is favored in acidic condition [26]. Under basic conditions on the other hand, the removal of phenolic compounds was not efficient even with an increase in electrolysis time. The influence of pH on the removal of TOC (Figure 3) was also conclusive, showing that at a pH of 1 the removal of TOC proceeded to 97%, with an initial value of 18200 mg L^{-1} and a final value of 553 mg L^{-1} . This behavior was verified before the electrochemical treatment at different pH values, where it was observed that the sample changed its color



FIGURE 2: Removal of phenolic compounds in pretreated industrial samples at different pH values (1, 7, and 14), under constant stirring, using BDD and Ti as anode and cathode. 2 A ($j = 0.32 \text{ A cm}^{-2}$) for 60 minutes of electrolysis were applied.

with the progression of the reaction (with agitation at 298K) during 2 hours (Figure 4). While at pH 14, the color of the solution was practically the same, at pH 7 and pH 1, the color in the solution disappeared. Similar results on the effect of the pH were obtained by Wei et al. [27] who evaluated the use of electrochemical technology as pretreatment of heavy oil refinery wastewater. Their results showed a similar effect of the pH, indicating that the better removal occurs under acidic medium, followed by neutral and alkaline conditions. The consistent pH effect observed in this work can be explained by considering that in an acidic environment oxygen evolution is inhibited, thus, improving the oxidation process [27]. The low efficiency of the process under alkaline conditions on the other hand, can be explained by considering that during the electrolysis, the creation of CO₂ allows the formation of carbonates and bicarbonates (4), well known scavengers of hydroxyl radicals [28] as represented by (5) [29]

$$CO_2 + NaOH \longrightarrow NaHCO_3$$

$$NaHCO_3 + NaOH \longrightarrow Na_2CO_3$$

$$\bullet OH + CO_3^{2-} \longrightarrow OH^- + CO_3^{--}$$
(4)

$$^{\bullet}\mathrm{OH} + \mathrm{HCO}_{3}^{-} \longrightarrow \mathrm{H}_{2}\mathrm{O} + \mathrm{CO}_{3}^{\bullet-}$$
⁽⁵⁾

In addition, an alkaline environment can reduce the overpotential for oxygen evolution [30], thus resulting in a low reaction efficiency.

3.3. Electrolysis with A Photoelectro-Fenton System. For the photoelectro-Fenton system, an initial phenolic compounds concentration of 3471 mg L^{-1} became a final concentration of 2.09 mg L⁻¹, demonstrating the effectiveness of the phenol degradation process with a removal of 99.9%. In this case the TOC removal (Figure 5) was not as significant as in the



FIGURE 3: TOC values before and after the electrochemical oxidation process using BDD, at different pH values (1, 7, and 14), applying 2 A (j = 0.32 A cm⁻²) of current over 2 hours in pretreated industrial samples.

case of the BDD approach, with only 25.7% removal after 120 minutes.

These results are in agreement with literature reports, where it has been demonstrated that the application of a photoelectro-Fenton process in water residues from refineries can produce 98.7% removal of phenol and 75.7% removal of COD, taking into account that the efficiency of the reaction can be improved in the photoelectro-Fenton process [28], which can also have synergistic photolysis effects. The results obtained using BDD were also consistent with the literature, where the removal of phenol has been reported to be 99.53% with a 96.04% removal of COD [8]. The feasibility of the use of the BDD in the treatment of complex wastewater effluents has also been demonstrated by Rocha et al., who obtained high efficiencies from the electrochemical oxidation process [31]. With these results, the electro-oxidation of phenol using boron-doped diamond is proven to be more effective in removing both phenol and TOC, in contrast to the photoelectron-Fenton system, where only a fourth of the total TOC content is removed. This study, therefore, supports BDD as a viable solution for eliminating phenol and other organic compounds from refinery wastewater.

4. Conclusions

The selective degradation of phenolic compounds in samples obtained from the hydrocarbon industry by electrochemical oxidation with BDD was successfully achieved. The degradation of phenolic compounds proceeded with a 97% of removal of TOC by applying a 2 A (j = 0.32 A cm⁻²) current for 2 hours at 297 K under constant stirring and acidic conditions. In addition, the use of BDD as an anode in the electro-oxidation of phenol in acidic conditions was found to be the best alternative for obtaining the highest removal of intermediates, in contrast to the photoelectro-Fenton system for which, following literature conditions, only 25.7% of TOC was removed. From these results, the use of BDD is



FIGURE 4: Images of industrial samples treated with BDD applying 2 A ($j = 0.32 \text{ A cm}^{-2}$) of current over 2 hours, with constant stirring at pH (a) 1, (b) 7, and (c) 14.



FIGURE 5: TOC values after 120 minutes of reaction time employing the photo-electron-Fenton process, using carbon fiber modified with TiO₂ in the presence of 120 mg L^{-1} of H_2O_2 and 0.5 mM $\text{Fe}(\text{SO}_4)_2$ at pH 3, with an application of radiation at 365 nm with a lamp of $0.71 \,\mu\text{W cm}^{-2}$. The solution was pre-saturated with oxygen.

confirmed as a viable approach for the elimination of recalcitrant organic contaminants in water effluents generated by the refineries.

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