The Box-Benkhen experimental design for the optimization of the electrocatalytic treatment of wastewaters with high concentrations of phenol and organic matter

Edison GilPavas, Alejandra Betancourt, Mónica Ángulo, Izabela Dobrosz-Gómez and Miguel Ángel Gómez-García

ABSTRACT

In this work, the Box-Benkhen experimental Design (BBD) was applied for the optimization of the parameters of the electrocatalytic degradation of wastewaters resulting from a phenolic resins industry placed in the suburbs of Medellin (Colombia). The direct and the oxidant assisted electro-oxidation experiments were carried out in a laboratory scale batch cell reactor, with monopolar configuration, and electrodes made of graphite (anode) and titanium (cathode). A multifactorial experimental design was proposed, including the following experimental variables: initial phenol concentration, conductivity, and pH. The direct electro-oxidation process allowed to reach ca. 88% of phenol degradation, 38% of mineralization (TOC), 52% of Chemical Oxygen Demand (COD) degradation, and an increase in water biodegradability of 13%. The synergetic effect of the electro-oxidation process and the respective oxidant agent (Fenton reactant, potassium permanganate, or sodium persulfate) led to a significant increase in the rate of the degradation process. At the optimized variables values, it was possible to reach ca. 99% of phenol degradation, 80% of TOC and 88% of COD degradation. A kinetic study was accomplished, which included the identification of the intermediate compounds generated during the oxidation process.

Key words | anodic oxidation, electro-oxidation process, kinetics, phenol

INTRODUCTION

A major fraction of pollutants resulting from the chemical industries is presented as wastewaters streams. In many cases, even if their low concentrations make their recovery economically unfounded, they are considered as an important source of pollution. The rising environmental concern, of both industrial and academic groups, has stimulated the development and diffusion of new technologies for the wastewaters treatment. Phenol is one of the most toxic and recalcitrant compounds present in the wastewaters resulting from the production process of resins, herbicides, pharmaceutical products, colorants, paints, etc., (Cravotto et al. 2005). The advanced oxidation processes (AOPs), based on hydroxyl radicals (·OH) generation, with high standard potential ($E^\circ = 2.8$ V), have attracted much attention during the last years mainly due to the high degradation capacity of numerous organic compounds (Katsumata et al. 2004; Rodríguez et al. 2005). Those species react in a non-selective way with the organic compounds, producing less pollutant compounds such as carboxylic acids, sometimes achieving even complete mineralization (total pollutant conversion to CO$_2$, water, and inorganic ions).
Between the AOPs, the electro-Fenton (EF) process is the most studied. It includes the formation of the hydroxyl radicals from H$_2$O$_2$ and Fe ions, in acid medium (Araña et al. 2001; Malato et al. 2007; Schwingel et al. 2007). This process is carried out in the electrolytic cells, which contain insoluble ions, generating free radicals, hydroxyls, H$_2$O$_2$ and catalysts which are increasing the available quantity of hydroxyl radicals (Goodridge & Scott 1995; Rajeshwar & Ibanez 1997; Chen 2004; Rodríguez et al. 2005; Oturan & Brillas 2007; Brillas et al. 2008a,b). Thus, the anodic oxidation implies the oxidation and rupture of chemical bonds of the toxic compounds, also by the hydroxyl radicals which are formed as follows:

\[
H_2O \rightarrow \cdot OH_{Ads} + H^+ + e^- \quad (1)
\]

\[
O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)
\]

In order to increase the oxidation power of the electro-generated H$_2$O$_2$, a small amount of an oxidation agent is frequently added to the solution. Its presence leads to the increase in the degradation rate of organic compounds, making them much more susceptible to the degradation by the electro-oxidation.

The response surface methodology (RSM) is the statistical technique which can be used to establish relationships between several independent variables and one or more dependent ones. The polynomial model can be developed using statistical experimental designs. The RSM technique optimizes multiple variables by the systematic variation of all variables in a well-designed experiment with a minimum number of them. The RSM optimization process involves the following steps: (1) performing statistically designed experiments; (2) estimating the coefficients of a mathematical model using regression analysis technique; and (3) predicting the response and checking the adequacy of the model. Among the available statistical design methods, the Box-Benkhen Design (BBD) is usually chosen for the purpose of response optimization. The BBD technique are presented elsewhere (Antony 2005; Montgomery 2005; Ryan 2007; GilPavas & Gómez-García 2009; Ray et al. 2009).

The main objective of this work was to optimize the operation conditions of the direct electrocatalytic treatment of wastewaters with high content of phenol and organic matters, resulting from a phenolic resins industry placed in the suburbs of Medellin (Colombia). To achieve this goal, the direct anodic oxidation method was used alone and assisted by different oxidant agents: Na$_2$S$_2$O$_8$, KMnO$_4$, or the Fenton reactant (EF). The efficiency of the electro-oxidation process was evaluated following the degradation rate of phenol, organic matter (Chemical Oxygen Demand, COD), and mineralization (Total Organic Carbon, TOC) during the treatment process. Data were studied by a BBD statistical analysis. At the optimized conditions, the effect of each oxidant agent was evaluated. A kinetic study was also undertaken, including the identification of the intermediate compounds generated during the oxidation process.

**MATERIALS AND METHODS**

**Samples**

The initial samples were taken directly from the wastewater stream of the phenolic resin industrial plant. Before analysis and treatment in the laboratory, they were kept refrigerated in order to avoid compounds degradation during the storage and the transportation. The wastewater presents a very high pollutant degree. Among many compounds, it is characterized by the presence of phenol in the concentration range 900–2,000 ppm. The main characteristics of the wastewater stream are presented in Table 1.

In order to obtain samples with different initial phenol concentrations for the evaluation of the electro-oxidation process, fractions of the former sample were diluted with extra pure water (obtained from Milli-Q system, 18 MΩ resistivity).

**Electro-oxidation cell**

A plexiglas 0.2 L batch jacketed cell was used for all experiments. It contains two vertical electrodes: one flat plate made of Ti, the cathode, having a total area of 55 cm$^2$.
and an effective reaction area of 40 cm²; and another, the anode, a cylinder made of graphite, with 34.55 cm² total area from which 25.13 cm² was effective for the reaction. Electrodes were connected in a monopolar arrangement. They were disposed vertically in the cell, with a 0.5 cm gap between them, and the current density of 25 mA/cm². Voltage was regulated with a BK-Precision (0–30 V, 0–5 A) source. The reaction mixture was stirred at 200 rpm, and the total reaction time was of 4 hours. Test temperature was controlled at 28°C by a Polyscience 712 thermostat connected to the jacket. The representation of the electro-oxidation cell is presented in Scheme 1.

### Analytical methods

The evolution of phenol and intermediate compounds, generated during the electro-oxidation process, was followed by High Pressure Liquid Chromatography (HPLC). A HPLC-UV, AGILENT, was used with the following parameters: mobile phase: acetonitrile–water–acetic acid (36–60–4), flow: 0.8 ml/min, lamp: tungsten-deuterium, column: ECLIPSE X DB-C18-5 μm, and retention time: 10 min. Standard methods were used for the quantitative analysis of COD, BOD₅, and TOC (Standard Methods 2005). The COD analyses were performed following the closed reflux method, with colorimetric measurements (method 5220D). Total organic carbon (TOC) was analyzed with a Shimadzu analyzer (model TOC-5,000A), method 5310D, and the BOD₅ measurements were performed following the respirometric method (5210B).

The efficiency of the treatment process was defined basing on the phenol degradation percentage (%DPh), COD, and TOC; each calculated using, for example for phenol, the following expression:

\[
\% \text{DPh} = \left(\frac{C_0 - C}{C_0}\right) \times 100
\]

where \(C_0\) and \(C\) correspond to the initial and final phenol concentrations, respectively.

### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>mg/L</td>
<td>1,600</td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>3,300</td>
</tr>
<tr>
<td>BOD₅</td>
<td>mg/L</td>
<td>957</td>
</tr>
<tr>
<td>BOD₅/COD</td>
<td>–</td>
<td>0.29</td>
</tr>
<tr>
<td>TOC</td>
<td>mg/L</td>
<td>1,450</td>
</tr>
<tr>
<td>pH</td>
<td>–</td>
<td>3.69</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm³</td>
<td>1.0017</td>
</tr>
<tr>
<td>Viscosity</td>
<td>cp</td>
<td>0.9384</td>
</tr>
<tr>
<td>Color</td>
<td>–</td>
<td>Transparent</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/cm</td>
<td>2.120</td>
</tr>
</tbody>
</table>

### Scheme 1

![Representation of the electro-oxidation cell.](https://iwaponline.com/wst/article-pdf/60/11/2809/447376/2809.pdf)
Experimental design and statistical analysis

The RSM was chosen and implemented to define the optimal operational conditions of the EC process. A multifactorial BBD was defined in order to evaluate the influence of several parameters including: the conductivity, pH, and the initial phenol concentration. The experiments were programmed using Statgraphics 5.1 (Statistical Graphics Corp 1999–2004). Thus, fifteen test with replica, were randomly made in order to avoid any systematic errors. From preliminary experiments (not presented here), three different levels (values) were chosen for each of three variables. Variable levels and codifications are presented in Table 2.

Variables were coded according to Equation (4):

\[ X_i = \frac{(x_i - x_{pc})}{\Delta x_i} \]  

(4)

where \( X_i \) is the code level, \( x_i \) is the uncoded value, \( x_{pc} \) corresponds to uncoded value at the central point, and \( \Delta x_i \) is the change value between levels (Montgomery 2005).

The statistical analysis was based on the analysis of variance (ANOVA), Pareto diagram, Box-Benkhen response surface plot, and the variation coefficients. Experimental data were analyzed using Statgraphics 5.1. For the response surface method, the experimental results were adjusted to a second order multivariable polynomial as presented in Equation (5):

\[ Y_i = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=1}^{3} \beta_{ij} X_i X_j \]  

(5)

where \( Y_i \) was the response variable: percentage of phenol degradation (%DPh); \( \beta_0, \beta_i, \beta_{ii}, \) and \( \beta_{ij} \) were the regression coefficients which corresponds to the intersect, lineal, quadratic, and interactions, respectively; and \( X_i \) and \( X_j \) are the independent variables. The quality of this model and its prediction capacity are related to the variation coefficient, \( R^2 \).

RESULTS AND DISCUSSION

The electro-oxidation process

The experimental results of the %DPh, obtained for each experiment and replica, for the conditions presented in Table 2, are given in Table 3.

It is possible to see that the highest observed value of %DPh was 88.5%, which corresponds to a conductivity of 6 mS/cm, pH 9.5, and the initial phenol concentration of 1,200 ppm (Table 3). The ANOVA results are presented in Table 4.

From the results presented in Table 4, it could be seen how the p value confirms the statistical importance of each factor: four of them (the conductivity, the initial phenol concentration, and their interactions: AA and CC) present values \( \leq 0.05 \), which implies that they have a truthfully effect on %DPh, with a confidence interval of 95%

Table 2 | Chosen variables levels from the experimental design

<table>
<thead>
<tr>
<th>Variable</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (CD) (mS/cm)</td>
<td>2</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>pH</td>
<td>7</td>
<td>8.3</td>
<td>9.5</td>
</tr>
<tr>
<td>Initial phenol concentration (C_i) (ppm)</td>
<td>800</td>
<td>1,200</td>
<td>1,600</td>
</tr>
</tbody>
</table>

Table 3 | The experimental results for the three variables and levels

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Conductivity, CD (mS/cm)</th>
<th>Initial phenol concentration, C_i (ppm)</th>
<th>Phenol degradation percentage (%DPh)</th>
<th>%DPh</th>
<th>%DPh replica</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>8.3</td>
<td>800</td>
<td>6.2</td>
<td>5.72</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>9.5</td>
<td>1,200</td>
<td>8.63</td>
<td>7.84</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>7.0</td>
<td>1,200</td>
<td>7.2</td>
<td>6.83</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>8.3</td>
<td>1,600</td>
<td>1.23</td>
<td>1.78</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>9.5</td>
<td>800</td>
<td>68.2</td>
<td>70.56</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>7.0</td>
<td>800</td>
<td>69.68</td>
<td>65.56</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>8.3</td>
<td>1,200</td>
<td>64.6</td>
<td>68.4</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>8.3</td>
<td>1,200</td>
<td>65.5</td>
<td>66</td>
</tr>
<tr>
<td>9</td>
<td>4</td>
<td>8.3</td>
<td>1,200</td>
<td>62.5</td>
<td>63</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>7.0</td>
<td>1,600</td>
<td>9.65</td>
<td>10.5</td>
</tr>
<tr>
<td>11</td>
<td>4</td>
<td>9.5</td>
<td>1,600</td>
<td>16.36</td>
<td>14.87</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>8.3</td>
<td>800</td>
<td>72.73</td>
<td>73.49</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>9.5</td>
<td>1,200</td>
<td>86.88</td>
<td>88.5</td>
</tr>
<tr>
<td>14</td>
<td>6</td>
<td>7.0</td>
<td>1,200</td>
<td>80.88</td>
<td>77.71</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>8.3</td>
<td>1,600</td>
<td>50.39</td>
<td>49.46</td>
</tr>
</tbody>
</table>
Conversely, the direct influence of pH on the phenol degradation rate was not observed in the studied range of pH (7–9.5). Such effect was also observed by us in some preliminary analysis (not shown here) and in the open literature by Bagotsky (2006).

Pareto diagram (Figure 1) allows to choose the factors having a significant influence on the phenol degradation by electro-oxidation. The selected factors correspond to all those which values overpass the inner vertical line. The vertical line corresponds to the T value in the T student distribution, with a 95% confidence and for 19 freedom degrees. Next, this value is compared to the values of each effect and interaction of analyzed factor. The comparison defines the statistical significance of each factor in the analyzed process. Thus, it is possible to see that the factors that have an influence on the degradation process are: the conductivity (CD), the initial concentration (Ci), the interaction CD–CD and the interaction Ci–Ci which are crossing the inner vertical line (Figure 1).

The %DPh is directly proportional to the CD (higher electrons transference and mobility in the reactive medium) but inversely proportional to Ci. If the solution is oversaturated, ions can not be fully attached (Figure 1). Similar results have been published by the other authors (Bagotsky 2006; Marques et al. 2008). Figure 2 presents the comparison of the observed and the predicted values obtained by a quadratic regression method.

As it could be seen, the data are adjusted to a straight line with a correlation factor $R^2$ equals to 0.9232 (Figure 2).

Several analyses were developed using the Box-Benkhen surface response method, at the fixed Ci values and varying the other two variables. Best results were obtained at Ci equal to 986 ppm. In Figure 3, a sample of the Box-Benkhen surface response diagram summarizes the effect of the studied variables: current density (CD) and pH at the optimized initial phenol concentration of 986 ppm.

It is possible to see that, at Ci constant, the %DPh increases significantly with the increase in conductivity and slightly with pH (Figure 3). Statistical analysis predicts the conditions for the maximum of %DPh (97%) which corresponds to: $C_i = 986$ ppm, $CD = 6$ mS/cm, and pH = 9.3. The quadratic regression model allows to obtain the Equation (6), as a function of the three factors involved in this study.

### Table 4 | ANOVA results for the phenol degradation results

<table>
<thead>
<tr>
<th>Factor</th>
<th>Square sum</th>
<th>Freedom degrees</th>
<th>Square average</th>
<th>F ratio</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Conductivity (CD)</td>
<td>19,224.5</td>
<td>1</td>
<td>19,224.5</td>
<td>154.48</td>
<td>0.0000</td>
</tr>
<tr>
<td>B: pH</td>
<td>181.104</td>
<td>1</td>
<td>181.104</td>
<td>1.46</td>
<td>0.2425</td>
</tr>
<tr>
<td>C: Initial concentration (Ci)</td>
<td>4,826.78</td>
<td>1</td>
<td>4,826.78</td>
<td>38.78</td>
<td>0.0000</td>
</tr>
<tr>
<td>AA</td>
<td>1,152.81</td>
<td>1</td>
<td>1,152.81</td>
<td>9.26</td>
<td>0.0067</td>
</tr>
<tr>
<td>AB</td>
<td>147.49</td>
<td>1</td>
<td>147.49</td>
<td>1.19</td>
<td>0.2899</td>
</tr>
<tr>
<td>AC</td>
<td>175.406</td>
<td>1</td>
<td>175.406</td>
<td>1.41</td>
<td>0.2498</td>
</tr>
<tr>
<td>BB</td>
<td>146.029</td>
<td>1</td>
<td>146.029</td>
<td>1.17</td>
<td>0.2923</td>
</tr>
<tr>
<td>BC</td>
<td>7.1442</td>
<td>1</td>
<td>7.1442</td>
<td>0.06</td>
<td>0.8132</td>
</tr>
<tr>
<td>CC</td>
<td>2,918.69</td>
<td>1</td>
<td>2,918.69</td>
<td>23.45</td>
<td>0.0001</td>
</tr>
<tr>
<td>Blocks</td>
<td>0.00560</td>
<td>1</td>
<td>0.00560</td>
<td>0</td>
<td>0.9947</td>
</tr>
<tr>
<td>Total error</td>
<td>2,364.55</td>
<td>19</td>
<td>124.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (corr.)</td>
<td>3,0772.9</td>
<td>29</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$R^2 = 92.32%$. 

Figure 1 | Pareto diagram for the phenol degradation process.
In order to improve the direct electro-oxidation process, three different oxidation agents (Fenton reactant, potassium permanganate, or sodium persulfate) were added to the reactive mixture. The optimal conditions obtained in section 3.1 were kept. The other conditions, such as the amount of the sample, the distance between the electrodes, the stirring velocity, the current density, and the reaction time, were the same of those in the section 2.2. COD and TOC kinetic studies were undertaken with the purpose of the evaluation of the efficiency of the assisted process. Additionally, for comparison, kinetics studies were evaluated separately for the direct electro-oxidation process and each oxidation agent by monitoring the phenol degradation percentage, COD, and TOC as a function of time, as proposed by Fogler (2006). The experimental results are presented comparatively in Figures 4, 5, and 6 and discussed below.

**Phenol degradation kinetics**

*Electro-oxidation process or oxidation agents.* Several experiments for phenol degradation were performed with electrolysis and some other with the presence of only an oxidation agent, without electrolysis. For Fenton reactant, KMnO4, and Na2S2O8, it was possible to reach a phenol degradation of 29, 7.5, and 3.6 percent, respectively. The organic matter degradation reaches ca. 8% with Fenton reactant; however, no activity was detected for the other two oxidation agents.

In the case of the electro-oxidation process (EQ), the %DPh increases with time reaching finally 88% at 240 minutes. The EQ is particularly fast during the first 60 minutes, period when the hydroxyl radical are formed (Figure 4). The evident accumulation of bubbles on the electrodes surface (probably containing oxygen and hydrogen) observed during the experiment increases the mass transfer resistance and leads to the decrease in the degradation rate, as also reported previously (Hurley & Masterton 1997; Zumdahl & Zumdahl 2000; Mollah et al. 2001, 2004).

$$\%DPh = -349.74 + 35.18\, CD + 40.51\, pH + 0.26\, C_i - 3.12\, CD^2 + 1.72\, CD \times pH - 0.006\, CD \times C_i - 2.85\, pH^2 + 1.9 \times 10^{-3}\, pH \times C_i - 1.24 \times 10^{-4}\, C_i^2$$

(6)

**Figure 2** | The comparison of observed and predicted values for the %DPh.

**Figure 3** | The effect of the CD and pH on %DPh, at the optimized initial phenol concentration ($C_i = 986$ ppm).

**Figure 4** | Phenol degradation kinetics for the electro-oxidation process (EQ), and the electro-oxidation assisted processes: EK, EP, and EF.
Electro-oxidation process assisted by KMnO₄: EK. For the EK process, 3.17 × 10⁻³ mol/l of KMnO₄ was added initially to the reactive solution. In this case, the %DPh reaches ca. 98% after 240 minutes (Figure 4). This effect can be explained by the presence of extra -OH radicals, which are formed according to the following equation:

\[ 4\text{MnO}_4^- + 2\text{H}_2\text{O} \rightarrow 4\text{HO}^- + 4\text{MnO}_2 + 3\text{O}_2 \]  (7)

The amount of KMnO₄ employed in this kind of process highly depends on the nature, concentration, structure, and molecular size of the pollutant. Despite of the high degradation activity, it is important to notice that some organic compounds can be adsorbed by the MnO₂ generated during the permanganate reduction process (Colthrust & Singer 1982; Lunn & Sansone 1994; Herrera et al. 2000). This implies that intermediate compounds just can change their oxidation state, without suffering a real oxidation process.

Electro-oxidation process assisted by Na₂S₂O₈: EP. At the zero reaction time, 8.4 × 10⁻⁴ mol/l of Na₂S₂O₈ was added to the reactive mixture. During the EP process, the %DPh achieves ca. 98% at 240 minutes of reaction (Figure 4). The synergetic effect of electrolysis and oxidant agent can be explained by the capacity of persulfate ion (S₂O₈²⁻) to form additional -OH radicals. In fact, the -SO₄⁻ radical are also very well known as highly oxidant compounds (Malato et al. 1999a, b). These two effects are illustrated by the Equations (8) and (9).

\[ \text{S}_2\text{O}_8^{2-} + e^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{OH}^- + \text{SO}_4^{2-} + \text{H}^+ \]  (8)

\[ \text{·SO}_4^- + \text{H}_2\text{O} \rightarrow \text{·OH} + \text{SO}_4^{2-} + \text{H}^+ \]  (9)

Electro-oxidation process assisted by the Fenton reactant: EF. At the beginning of the experimental test, 4.48 × 10⁻³ mol/l of Fe³⁺ (FeSO₄·7H₂O) and 0.118 mol/l of H₂O₂ were added into the reactive mixture. After 240 minutes, phenol degradation higher than ca. 99% was detected (Figure 4). It is possible to see that the EF process is significantly faster that EK and EP processes (Figure 4). The Fenton reactant highly accelerates the degradation process. This can be explained by the -OH radicals assistance formation from H₂O₂ and Fe²⁺, as presented in Equations (10) and (11) (Araña et al. 2001; Oturan & Brillas 2007).

\[ \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \]  (10)

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{·OH} \]  (11)

From the kinetics analysis (not presented here), it was found that, for the EF, EP, EK, and EQ processes, the correlations between ln(Ct/C₀) and the reaction time were linear. This is a typical first-order plot. The kinetic constants were equals to 0.384, 0.201, 0.0172, and 0.0105 min⁻¹, respectively.
**COD and TOC degradation kinetics**

The kinetics results of COD and TOC obtained by direct electro-oxidation (EQ), and the assisted process EK, EP, and EF, are presented comparatively in Figures 5 and 6, respectively. During the EQ process, the COD and TOC are degraded to ca. 52% and 38%, respectively. The degradation rate is significantly higher during the first 120 minutes. We expect that the graphite electrode (anode) can promote the formation of intermediate compounds. Moreover, the rate of formation of hydroxyl radicals became slower, as proposed by Feng & Li (2003). The biodegradability of the wastewater increases in 13% (up to 0.328), in relation to the original value. However, it is still out of the range for a biological treatment. For the EK process, the COD and TOC are both degraded to ca. 58%. The biodegradability increases up to 0.421, which corresponds to an intermediate value in the biodegradability range (0.3 – 0.5). The EP process allows reaching ca. 64% COD and ca. 66% TOC degradation. The biodegradability attains now 0.623 which implies that the treatment highly recuperates the wastewater. Finally, in the EF process, COD and TOC reach the highest degradation values: 88% and 80%, respectively. The biodegradability reaches 0.943 in relation with the initial value, implying that the wastewater is highly biodegradable.

From the results presented in Figures 5 and 6, it was found that, for all processes, the COD and the TOC data of ln(C/Co) and the reaction time adjust properly to a first-order model (not presented here). For the COD degradation, the kinetic constants for the EQ, and the assisted EK, EP, and EF were equals to 0.0035, 0.004, 0.0046, and 0.0083, respectively. In the case of TOC, the same processes have, in that order, as kinetic values: 0.0022, 0.0038, 0.0044, 0.0059 min⁻¹.

**The oxidation sequence**

The oxidation process was followed by chromatography, which made possible to detect the different products formed during the oxidation process: catechol, hydroquinone, and the acids: carboxilic, maleic, malonic, fumaric, and acrilic. It was possible to follow the formation of those compounds at different reaction time (not presented here). From those results, it is possible to propose a sequence for the phenol electro-oxidation process, as illustrated in Figure 7.

In the case of phenol degradation, the oxidative effect of ·OH radicals transforms phenol first into catechol and hydroquinone, which are consequently oxidized into carboxilic, maleic, malonic, fumaric, and acrilic acids. Next, they react to form acetic and oxalic acids. During the EF process, the acetic acid is directly oxidized into CO₂, by the ·OH radicals formed from reaction (11). The oxalic acid is more resistant to the oxidation process, remaining in the wastewater or even forming some other complexes with Fe⁺³ (Boye et al. 2002).

**CONCLUSIONS**

The application of the response surface methodology (RSM) and the Box-Benken Design (BBD) technique let to optimize the parameters of electro-oxidation wastewaters...
treatment resulting from a phenolic resins industry placed in the suburbs of Medellin (Colombia). The EQ process is an effective method for the phenol degradation. The optimal operation conditions for the EQ process were established as following: the conductivity of 6mS/cm, pH 9.3 and the initial phenol concentration of 986 ppm. At the estimated conditions, the EQ process allowed to reach ca. 88% of phenol degradation, 38% of mineralization (TOC), 52% of COD degradation, and an increase in water biodegradability of 13%. The addition of the oxidant agent (Fenton reactant, potassium permanganate, or sodium persulfate) let to a significant increase in the rate of the degradation process, being the best results for the electro-oxidation process assisted with the Fenton reactant: 99% of phenol degradation, 79% of TOC, 88% of COD degradation, and a biodegradability of 0.943. This last value implies that the wastewater is highly biodegradable, fitting the Colombian environmental regulations for the Medellin city (local law 1594/1984).

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