Intensified-Fenton process for the treatment of phenol aqueous solutions
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ABSTRACT
An intensified-Fenton process for the treatment of phenol aqueous solutions has been studied as a continuous catalytic wet hydrogen peroxide oxidation system. This process consists of coupling the catalytic activity of a heterogeneous Fenton-like catalyst with the homogeneous contribution of its dissolved iron species. Agglomerated mesoporous SBA-15 silica-supported iron oxide (Fe₂O₃/SBA-15) material was used as heterogeneous catalyst. The influence of the reaction temperature and the initial hydrogen peroxide dosages was studied in order to minimize the operation cost of the process. The catalytic performance of the process was assessed in terms of total organic carbon (TOC) and hydrogen peroxide conversions. Likewise, the stability of the solid Fenton-like catalyst was also evaluated in terms of the dissolved iron species. The increase of the reaction temperature enhanced the TOC conversion and reduced the iron leaching from the heterogeneous catalyst. These results were related to the degradation of oxalic acid as responsible for iron extraction by formation of soluble stable iron complexes into the aqueous medium. Finally, the use of a moderate hydrogen peroxide concentration (2.6 g/L) and milder temperatures (80–120 °C) has led to remarkable results of TOC and phenol reductions as well as oxidant efficiency through the intensified-Fenton process.

Key words | Fenton, fixed bed reactor, intensified process, iron leaching, phenol, wet peroxide oxidation

INTRODUCTION
Advanced oxidation processes have emerged as an interesting alternative for the destruction of organic pollutants in industrial wastewaters (Saharan et al. 2014). These processes involve the generation of nonselective and highly reactive hydroxyl radicals, which are the strongest oxidant ($E_0 = 2.8$ V) after fluorine. The use of hydrogen peroxide as precursor of hydroxyl radicals for the oxidation of hazardous organic pollutants has been deeply studied in literature as wet hydrogen peroxide oxidation (WHPO) (Yan et al. 2013). Unlike other wet oxidation processes such as wet air oxidation or ozonation, WHPO takes advantage of employing hydrogen peroxide as liquid oxidant, avoiding gas–liquid mass transfer limitations. The relatively mild operating conditions of WHPO ($T = 80–120$ °C and $P_{\text{air}} = 1–5$ bar) have made this technology quite promising in terms of low energy consumption. Additionally, the generation of hydroxyl radicals from hydrogen peroxide can be increased by presence of transition metals with redox properties (Karpinska et al. 2014). The Fenton catalytic system based on Fe(III) or Fe(II) salts and H₂O₂ has been very effective for the oxidation of recalcitrant organic pollutants (Mitsika et al. 2013). Numerous works have been carried out in order to optimize the operating conditions (Su et al. 2011; Vallejo et al. 2014). The main weaknesses of homogeneous Fenton processes are the strict control of the pH (2.5–3.5) to guarantee a high catalytic performance and the recovery of the iron metal ions from the treated effluent which also generate a metallic sludge that needs further treatment. The use of heterogeneous iron-containing catalysts offers a practical alternative to conventional homogeneous catalysts (Calleja et al. 2005; Melero et al. 2006; Karthikeyan et al. 2011; Cleveland et al. 2014). Among these materials, mesoporous silica SBA-15-supported iron oxides of adjustable pore size and thick pore walls have shown remarkable catalytic properties and hydrothermal stability. These mesostructured catalysts have demonstrated high catalytic activity and low deactivation by metal leaching for
the catalytic oxidation of phenol in batch experiments (Melero et al. 2006) and fixed bed reactor (FBR) (Martínez et al. 2007) as well as for the treatment of real wastewater streams coming from different industries (Pariete et al. 2010, 2013).

This work is dealing with an intensified-Fenton process by coupling of heterogeneous and homogeneous contribution of agglomerated mesoporous SBA-15 silica-supported iron oxide (Fe$_2$O$_3$/SBA-15) catalyst. This process consists of a catalytic FBR and a stirred tank reactor (STR) in a continuous recirculation mode. This system is considered an innovative process which can bring significant benefits in terms of the efficiency of heterogeneous catalysts for wastewater treatment by Fenton-like processes. This intensified-Fenton process takes advantage of the iron dissolved from the heterogeneous catalyst for further oxidation by homogeneous Fenton reactions in the STR. The reaction temperature and the dosage of hydrogen peroxide were studied for the degradation of phenol aqueous solutions as the most influencing variables in the economy of Fenton processes.

**METHODS**

**Catalyst preparation and characterization**

Powder material (Fe$_2$O$_3$/SBA-15) was initially synthesized following the procedure described in literature (Calleja et al. 2005). Thereafter, it was agglomerated by extrusion using sodium bentonite and synthetic methylcellulose polymer as binders as described elsewhere (Martínez et al. 2007). The characterization data revealed the hexagonal arrangement of mesostructured SBA-15 material as well as the presence of iron oxide as crystalline hematite entities. The resultant agglomerated catalyst using 25 wt% of bentonite provides ca. 294 m$^2$/g of specific surface area with a narrow pore diameter centred at 7.9 nm and 14 wt% of iron content.

**Intensified-Fenton catalytic runs**

Catalytic runs were performed in a novel experimental setup (Figure 1) designed for the continuous treatment of polluted effluents by integrating a catalytic FBR operating in up-flow with an autoclave operating as continuous STR. The use of both reactors is considered an innovative system to promote further oxidation in the STR by homogeneous Fenton reactions as iron leaching cannot be completely discarded in most of the heterogeneous Fenton catalysts. In this sense, the STR collects the feeding phenolic aqueous solution and the treated stream coming from the catalytic FBR. The agglomerated Fe$_2$O$_3$/SBA-15 solid catalyst was located in the tubular FBR (30 cm long and 2 cm i.d.).

Typically, the phenol aqueous solution (1 g/L) with a pH about 5.5 was fed to the STR with a flow rate ($F_f$) of 0.25 L/h. At the same time, the liquid solution of the STR was pumped
to the FBR through the recirculation loop with a flow rate ($F_R$) of 1.25 L/h. The catalyst mass located in the FBR was 5 g. Under these operation conditions, the overall residence time ($\tau$), calculated according to Equation (1), was 1.2 min

$$\tau = \frac{W_{\text{cat}}}{\rho \cdot F_R}.$$  

(1)

The temperature of the STR ($T_{\text{STR}}$) was set to 80 °C and the liquid level to 0.5 L as working volume. As heterogeneous Fenton catalysts normally show lower kinetic rates than homogeneous iron species (Barona et al. 2015), the temperature in the FBR ($T_{\text{FBR}}$) was increased into the range of 100–160 °C. A constant air flow of 0.15 mL/min was supplied to pressurize the catalytic system ($P_{\text{O}_2} = 2$ bar). The hydrogen peroxide dosage in the feeding solution was varied from 1.3 to 5.1 g/L, which corresponded to 60 and 235%, respectively, of the stoichiometric amount for carbon mineralization according to Reaction (2). This reaction takes into account the oxygen provided by the air flow as an extra source of oxidant to enhance the oxidation process

$$\text{C} + \text{H}_2\text{O}_2 + 1.5\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$  

(2)

### Analytical methods

The catalytic activity of the oxidation treatment was evaluated by monitoring several parameters in the outlet aqueous solution, such as the phenol and the total organic carbon (TOC) removal, the hydrogen peroxide conversion, pH and the iron leaching from the catalyst to the treated solution. The TOC content was analysed using a combustion/non-dispersive infrared gas analyser model TOC-V (Shimadzu). Phenol and other oxidation byproducts were quantified by means of high-performance liquid chromatography (HPLC) (Varian Prostar) equipped with a Waters Spherisorb column and an ultraviolet detector adjusted to 215 nm. Ultra-pure water acidified with H$_3$PO$_4$ up to pH equal to 2.7 was employed as mobile phase. Hydrogen peroxide conversion was determined by iodometric titration. Iron content in the treated solution was measured by inductively coupled plasma-atomic emission spectroscopy analysis collected in a Varian VISTA AX system. The performance of the reaction was studied following the parameters described by Equations (3)–(5)

$$\text{TOC conversion} \quad X_{\text{TOC}}(\%) = \frac{[\text{TOC}]_{\text{inlet}} - [\text{TOC}]_{\text{outlet}}}{[\text{TOC}]_{\text{inlet}}} \times 100.$$  

(3)

Oxidant consumption. $X_{\text{H}_2\text{O}_2}(\%) = \frac{[\text{H}_2\text{O}_2]_{\text{inlet}} - [\text{H}_2\text{O}_2]_{\text{outlet}}}{[\text{H}_2\text{O}_2]_{\text{inlet}}} \times 100.$  

(4)

Oxidant efficiency $\eta = \frac{\text{Theoretical consumption of H}_2\text{O}_2 \text{ according to reaction (2)}}{\text{Real consumption of H}_2\text{O}_2} \times 100.$  

(5)

### RESULTS AND DISCUSSION

Several variables were assessed in a previous work for the degradation of a model phenol solution (Martínez et al. 2008). The influence of the residence time was evaluated by variation of the feed flow rate and the catalyst loading. It was observed that the catalytic performance in terms of TOC and phenol degradation can be enhanced by the increasing of the residence time. Likewise, the catalytic performance was improved by homogeneous Fenton reactions. This fact was demonstrated by the increase of the TOC conversion when the temperature in the STR was increased from 40 to 80 °C. The improvement of performance was due to the activity of dissolved iron species in the STR. Higher temperatures were not used in order to prevent excessive thermal decomposition of hydrogen peroxide in the STR, where the feeding aqueous solution of phenol and hydrogen peroxide were introduced. Finally, the use of air and hydrogen peroxide simultaneously as oxidants was considered a beneficial feature to promote the oxidation of phenol, as it has been also reported in literature (Rivas et al. 1999; Pignatello et al. 2006). However, in this preliminary work, the influence of the FBR reaction temperature and the inlet hydrogen peroxide concentration on the overall catalytic performance and efficiency of the oxidant were not studied. Both variables are considered crucial points on the operating costs of conventional Fenton processes. Likewise, the stability of the catalyst under different operation conditions of temperature and oxidant concentration needs to be addressed in order to assess the feasibility of the heterogeneous catalyst in commercial applications.

### Influence of temperature in the heterogeneous FBR

The temperature in the FBR was varied from 100 to 160 °C, keeping constant the rest of operation conditions. It must be pointed out that the oxidation reaction rate is obviously
increased by the increase of temperature, but also the use of high temperatures might reduce the efficiency of the hydrogen peroxide due to its thermal decomposition to oxygen and water (Ovejero et al. 2001). In this study, the influence of the temperature in the FBR was carried out in order to evaluate its effect on phenol mineralization as well as oxidant efficiency.

Table 1 shows phenol, TOC and oxidant conversions, iron leaching concentration, pH and oxidant efficiency of the outlet effluent for the four studied temperatures at steady-state. The highest temperature (160 °C) showed the best catalytic performance with a TOC reduction of ca. 78%, and almost complete phenol removal (98–99%). It must be noteworthy that the increase of temperature did not produce a decrease of the oxidant efficiency. These results could be attributed to the low residence time of the intensified-Fenton process (1.2 min). The thermal decomposition of hydrogen peroxide at short residence times seems to be of the same extent in the range of temperatures under study (100–160 °C). Nevertheless, low oxidant efficiencies were obtained (0.35–0.38), indicating undoubtedly certain decomposition or non-efficient use of the hydrogen peroxide. However, probably the most remarkable result of this study was the decrease of the iron leaching concentration with the temperature. Note that the iron concentration decreased to 0.2 mg/L for 160 °C as compared with 13 mg/L for 100 °C.

It has been discussed in literature that the iron leaching from heterogeneous catalysts can be attributed to different factors. The acid and oxidizing conditions of Fenton reactions normally promotes the leaching of the iron species (Lázar et al. 2004). Moreover, the extraction capacity of certain aromatic-like compounds as well as their oxidized byproducts to form soluble metal complexes has also been reported (Santos et al. 2005; Feng et al. 2006). To elucidate whether the catalyst stability is influenced by this factor, the byproducts composition of the treated effluent was monitored. The concentration of phenol and different byproducts at the steady-state for each temperature reaction is shown in Figure 2.

It was observed that the concentration of phenol and primary aromatic byproducts like catechol and hydroquinone were low and they did not undergo any change as the temperature of the FBR increased. Among the following organic acid byproducts, maleic acid also displayed a low concentration. In contrast, shorter-chain refractory carboxylic acids, such as oxalic and acetic acids, showed different trends as the temperature increased. Oxalic acid decreased from 120 to 30 mg/L, whereas the acetic acid concentration increased from 50 to 175 mg/L with the increase of temperature from 100 to 160 °C in the FBR. Numerous works in literature have reported a double route for the maleic acid oxidation in the oxidation of phenol (Zazo et al. 2006; Zhou et al. 2011). One of them is the oxidation of maleic acid to oxalic acid with following decarboxylation to formic acid. The other one is based on previous decarboxylation of maleic acid to acrylic acid and further oxidation to malonic acid and final decarboxylation to acetic acid. The increase of temperature promotes a higher oxidation degree and mineralization of residual carboxylic acids. Thus, the oxalic acid concentration decreased as result of oxidation to formic acid and decarboxylation, as revealed by the increase of TOC conversion (see Table 1). On the other hand, the acetic acid increased as the final acid of the maleic-acrylic-malonic oxidation route and one of the most refractory carboxylic acids. In addition, it can be seen that the pH of the treated effluent became less acid, which

Table 1 | influence of the fixed bed reactor temperature at steady-state conditions. Operating conditions: \( F_r = 0.25 \text{ L/h}; \ F_S = 1.25 \text{ L/h}; \ W_{CAT} = 5 \text{ g}; \ [\text{Phenol}]_0 = 1 \text{ g/L}; \ [\text{H}_2\text{O}_2] = 5.1 \text{ g/L}; \ T_{STR} = 80 \text{ °C}; \ P_{O2} = 2 \text{ bar} \)

<table>
<thead>
<tr>
<th>( T_{FBR} ) (°C)</th>
<th>( X_{TOC} ) (%)</th>
<th>( X_{phenol} ) (%)</th>
<th>( X_{maleic} ) (%)</th>
<th>[Fe]leaching (mg/L)</th>
<th>pH</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>63.9</td>
<td>98.9</td>
<td>70.4</td>
<td>12.6</td>
<td>3.5</td>
<td>0.38</td>
</tr>
<tr>
<td>120</td>
<td>66.2</td>
<td>98.6</td>
<td>80.8</td>
<td>9.5</td>
<td>3.2</td>
<td>0.35</td>
</tr>
<tr>
<td>140</td>
<td>72.0</td>
<td>99.2</td>
<td>85.1</td>
<td>5.5</td>
<td>3.4</td>
<td>0.36</td>
</tr>
<tr>
<td>160</td>
<td>78.2</td>
<td>99.5</td>
<td>88.6</td>
<td>0.2</td>
<td>4.1</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Figure 2 | influence of the FBR temperature on the byproducts composition of the treated effluent at steady-state conditions. Operating conditions: \( F_r = 0.25 \text{ L/h}; \ F_S = 1.25 \text{ L/h}; \ W_{CAT} = 5 \text{ g}; \ [\text{Phenol}]_0 = 1 \text{ g/L}; \ [\text{H}_2\text{O}_2] = 5.1 \text{ g/L}; \ T_{STR} = 80 \text{ °C}; \ P_{O2} = 2 \text{ bar} \).
clearly indicated the progress of the mineralization of final carboxylic acids as the temperature increases.

Interestingly, a clear relationship can be found between the iron leaching and the concentration of oxalic acid in the outlet effluent (Figure 3). The concentration of iron significantly decreased as the concentration of oxalic acid was also reduced. These results seem to indicate that a larger extension of the mineralization degree, as it can be inferred from the decrease of refractory oxalic acid concentration and the increase of TOC conversion and pH of the treated effluent, is producing less catalyst deactivation by leaching. This behaviour is also in agreement with the conclusions of other works, where the presence of oxalic acid also showed an important impact on the catalyst stability (Zazo et al. 2006).

To conclude, the increase of temperature in the FBR up to 160 °C improved the performance of the intensified-Fenton process up to 78% of TOC reduction. The iron leaching was also significantly reduced until values of 0.2 mg/L. The intensified-Fenton process took advantage of the homogeneous Fenton process or WHPO at mild reaction temperature (80 °C) in the STR. In addition, the resulting oxidation byproducts, such as oxalic acid, have shown an important effect on the iron leaching by the formation of soluble iron complexes.

Influence of hydrogen peroxide dosage

The dosage of the hydrogen peroxide and the ratio between iron and hydrogen peroxide concentrations are crucial in the efficacy of conventional homogeneous Fenton process (Pera-Titus et al. 2004). In this work, the oxidant concentration was set to 5.1, 3.8, 2.6, and 1.5 g/L. In this sense, the efficiency of the oxidant for the phenol mineralization is a key parameter for the economy of the process in terms of operation costs. Table 2 shows the catalytic results of the different initial hydrogen peroxide concentrations.

The existence of an optimal concentration of hydrogen peroxide for Fenton-type reactions has been deeply discussed in literature (Riaño et al. 2014). This optimal concentration depends on the wastewater nature and the ratios of iron or pollutant to hydrogen peroxide concentrations. A high excess of hydrogen peroxide concentration can lead to scavenging reactions of hydroxyl radicals as indicated in Reaction (6), decreasing the oxidant efficiency (Babuponnum-sami & Muthukumar 2014)

\[
{\text{H}_2\text{O}_2} + \text{HO}^* \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \tag{6}
\]

In this study, it has been observed that the decrease of oxidant dosage up to 2.6 g/L does not affect the catalytic performance of the process in terms of TOC and phenol conversions, reaching values of ca. 64–68% and 98% for TOC and phenol reductions, respectively. However, taking into account the conversion of hydrogen peroxide and the resulting oxidant efficiency, the use of 2.6 g/L of hydrogen peroxide displayed the highest oxidant efficiency (\(\eta = 0.63\)). These results seem to indicate a better use of the oxidant when moderate dosages of hydrogen peroxide were used. The decrease of hydrogen peroxide to lower concentrations (1.5 g/L) reduced dramatically the catalytic performance of the intensified-Fenton process with a low 15% of TOC degradation and complete oxidant conversion. These results evidence a remarkable reduction of the oxidant efficiency. This fact was attributed to its partial and less effective consumption in the STR, where the feeding aqueous solution with hydrogen peroxide is introduced.

<table>
<thead>
<tr>
<th>([\text{H}_2\text{O}_2]) (g/L)</th>
<th>(X_{\text{TOC}}) (%)</th>
<th>(X_{\text{Phenol}}) (%)</th>
<th>(X_{\text{H}_2\text{O}_2}) (%)</th>
<th>([\text{Fe}]_{\text{leached}}) (mg/L)</th>
<th>pH</th>
<th>(\eta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>66.2</td>
<td>98.6</td>
<td>80.8</td>
<td>9.5</td>
<td>3.2</td>
<td>0.35</td>
</tr>
<tr>
<td>3.8</td>
<td>65.9</td>
<td>98.1</td>
<td>89.4</td>
<td>10.2</td>
<td>3.2</td>
<td>0.4</td>
</tr>
<tr>
<td>2.6</td>
<td>68.7</td>
<td>98.8</td>
<td>92.8</td>
<td>10.7</td>
<td>3.3</td>
<td>0.63</td>
</tr>
<tr>
<td>1.5</td>
<td>14.6</td>
<td>88.2</td>
<td>100</td>
<td>13.0</td>
<td>3.0</td>
<td>0.25</td>
</tr>
</tbody>
</table>

![Figure 3](https://iwaponline.com/wst/article-pdf/71/3/359/469845/wst071030359.pdf)
and mixed with the recirculating stream coming from the catalytic FBR.

**CONCLUSIONS**

Innovative intensified-Fenton process based on the catalytic activity of heterogeneous Fenton-like catalyst (Fe$_2$O$_3$/SBA-15) and additional homogeneous contribution of its dissolved iron species has been evaluated for the treatment of phenol solutions. The increase of temperature in the heterogeneous catalytic FBR up to 160 °C has shown a significant increase of the overall catalytic performance in terms of TOC reduction. Moreover, the iron leaching of the catalyst was noticeably reduced as a result of the oxalic acid degradation byproducts able to produce the iron extraction by formation of soluble metal complexes in the aqueous solution. This intensified-Fenton process has provided remarkable results of TOC conversion and catalyst stability at 120 °C and moderate hydrogen peroxide dosages (2.6 g/L), which are critical variables to minimize the operation costs of Fenton processes for industrial applications.

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**REFERENCES**


Riaño, B., Coca, M. & García-González, M. C. 2014 Evaluation of Fenton method and ozone-based processes for colour and

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