Catalytic wet hydrogen peroxide oxidation of a petrochemical wastewater
M. I. Pariente, J. A. Melero, F. Martínez, J. A. Botas and A. I. Gallego

ABSTRACT
Continuous Catalytic Wet Hydrogen Peroxide Oxidation (CWHPO) for the treatment of a petrochemical industry wastewater has been studied on a pilot plant scale process. The installation, based on a catalytic fixed bed reactor (FBR) coupled with a stirred tank reactor (STR), shows an interesting alternative for the intensification of a continuous CWHPO treatment. Agglomerated SBA-15 silica-supported iron oxide (Fe₂O₃/SBA-15) was used as Fenton-like catalyst. Several variables such as the temperature and hydrogen peroxide concentration, as well as the capacity of the pilot plant for the treatment of inlet polluted streams with different dilution degrees were studied. Remarkable results in terms of TOC reduction and increased biodegradability were achieved using 160°C and moderate hydrogen peroxide initial concentration. Additionally, a good stability of the catalyst was evidenced for 8 hours of treatment with low iron leaching (less than 1 mg/L) under the best operating conditions.

Key words | fixed bed reactor, petrochemical wastewater, pilot plant scale, SBA-15, wet peroxide oxidation

INTRODUCTION
Industrial plants generate increasing amounts of wastewater, contaminated with toxic and hazardous organic compounds for biological treatments, which cause severe problems for the environment. Among these pollutants can be pointed out a wide variety, such as aromatic and aliphatic hydrocarbons, different halogenated, sulphur and nitrogen-containing organic derivatives or even heavy metals in form of cyanides and other organic complexes (Bautista et al. 2008). Depending on the hazardous nature and concentration, several technologies are proposed for their separation or degradation (Busca et al. 2008). In the particular case of aromatic compounds, the separation can be accomplished by membrane-based solvent extraction, membrane pervaporation, adsorption, extraction or steam distillation. The presence of toxic and hazardous substances often forces the application of degradation-based technologies, such us supercritical water oxidation (SCO), non catalytic or catalytic wet air oxidation (WAO and CWAO, respectively), or the so-called advanced oxidation processes (AOPs) based on different chemical oxidants (ozone or hydrogen peroxide) and the presence or absence of catalysts at mild temperature and pressure conditions. One of the most known catalytic systems is the Fenton process which multiplies the powerful oxidant effect of hydrogen peroxide by the dissolution of metallic iron salts (Gogate & Pandit 2004a,b). These AOPs processes are characterized by the generation of highly reactive hydroxyl radicals (HO·) which have a high oxidant power and exhibit a low selectivity in the oxidation of any organic compound (Neyens & Baeyens 2003). Catalytic Wet Hydrogen Peroxide Oxidation (CWPO) as adapted Fenton catalytic system at temperatures and pressures slightly higher than atmospheric ones have been aim of intense development in order to increase the efficiency of conventional Fenton systems (Caudio et al. 2007; Martinez et al. 2007; Bautista et al. 2008). doi: 10.2166/wst.2010.875
Catalytic Wet Air Oxidation (CWAO) and Catalytic Wet Hydrogen Peroxide Oxidation (CWHPO) have demonstrated high efficiency for the treatment of agro-food and industrial effluents as well as sewage sludges (Debellefontaine et al. 1996; Bhargava et al. 2006), although the intensive energy requirements and hydrogen peroxide consumptions are some of the most common drawbacks of CWAO and CWHPO, respectively. Unlike CWAO, in which the degradation rate is strongly limited by the mass transfer of molecular oxygen from the gas to the liquid phase, CWHPO takes advantage of employing hydrogen peroxide as liquid oxidant which avoids gas-liquid phase, CWAO and CWHPO, respectively. Unlike CWAO, in which the degradation rate is strongly limited by the mass transfer of molecular oxygen from the gas to the liquid phase, CWHPO takes advantage of employing hydrogen peroxide as liquid oxidant which avoids gas-liquid mass transfer restrictions. Wastewaters from petroleum extraction, refining and chemical processing have been successfully treated with a homogeneous Fenton system under ambient conditions of pressure and temperature (López et al. 1999). These authors tested the efficiency of this process for the treatment of two different wastewater samples, one from oil production operations and the other one from a petrochemical plant. The treated effluents still contained hazardous concentrations of m-cresol, 2-chlorophenol, methyl-tert-butyl-ether (MTBE) and volatile aromatics (benzene, toluene, ethylbenzene and xylene), but a significant degradation of the organic pollution (COD degradation over 90%) was observed in relatively short periods of time under discontinuous batch treatments.

The use of solid catalysts by immobilization of the active metals over an inert support offers a practical solution to the typical drawbacks of homogeneous Fenton-like systems applied under CWHPO operating conditions: i) additional flocculation-coagulation and sedimentation processes to avoid additional metal pollution of the treated effluent by separation of dissolved iron species as iron sludges, and ii) a strict control of pH during the oxidation process (c.a. 2.5 – 3) to ensure the optimal catalytic performance of the homogeneous Fenton’s reagent. The most demanding properties of solid catalysts are addressed to increase its surface area, to minimize the metal sintering, to improve its chemical stability, and to govern the useful lifetime of the catalyst, in order to achieve high degradation rates and low catalyst deactivation (Matatov-Meytal & Sheintuch 1998). Solid catalysts may, in principle, be easily used in catalytic packed bed reactors, avoiding additional operation units for the recovery of the homogeneous metal salts dissolved in the treated effluent. The design of iron and/or copper-containing heterogeneous catalysts supported over zeolitic materials (Melero et al. 2004), mesostructured materials (Calleja et al. 2005) and pillared clays (Caudo et al. 2007) has attracted the interest of many researchers.

The aim of this research is the degradation of a petrochemical wastewater by a continuous Catalytic Wet Hydrogen Peroxide Oxidation (CWHPO) process on an intensified pilot plant. The wastewater selected for this study is currently pre-treated by a wet air oxidation process under high temperature and pressure conditions. The wet oxidation effluent, along with all other production facility wastewaters, is subsequent treated by an enhanced biological process based on the PACT technology, which consist on the addition of powdered activated carbon to an aerobic biological treatment that provides a synergistic effect on the performance of the treatment (Pedrerol et al. 2002). The substitution of the WAO process by a CWHPO technology results in a significant challenge of decreasing the high temperature and pressure used in the WAO process and the improvement of the treatment efficiency. In basis on the promising results of agglomerated Fe₂O₃/SBA-15 catalyst as solid Fenton-like catalyst for the degradation of phenolic aqueous solutions in a continuous fixed bed reactor (Martínez et al. 2007, 2008), this catalysts has been selected for the treatment of the petrochemical wastewater by Catalytic Wet Hydrogen Peroxide Oxidation using an intensified process that integrate a catalytic fixed bed reactor (FBR) and a continuous stirred tank reactor (CSTR) on a pilot plant scale. Under this intensified concept of CWHPO, several operating conditions such as the temperature of the catalytic fixed bed reactor and the influence of the initial hydrogen peroxide concentration were studied with the purpose of assessing the capacity of this installation for the treatment of diluted wastewater as first approach of plausible application of CWHPO for the treatment of petrochemical wastewaters.

METHODS
Catalyst preparation and characterization
Powder material (Fe₂O₃/SBA-15) was initially synthesized following the procedure described in literature.
Thereafter, it was agglomerated by extrusion using sodium bentonite and synthetic methylcellulose polymer as binders as described elsewhere (Martínez et al. 2007; González-Velasco et al. 1999). Finally, shaped-rod pellets of 2 mm were dried for 3 days under controlled temperature and humidity, and calcined in air at 650°C for 2 hours with a slow ramp of temperature. This catalyst exhibits the typical hexagonal arrangement of mesostructured SBA-15 material, as well as the presence of iron oxide as crystalline hematite entities. The agglomerated catalyst with 25 wt% of bentonite shows BET surface area of ca. 294 m²/g with a narrow pore diameter centred at 7.9 nm and iron content of 14 wt%.

**Catalytic wet hydrogen peroxide oxidation reactions**

Catalytic wet hydrogen peroxide oxidation of a petrochemical industry wastewater has been performed in the experimental set-up shown in Figure 1. This installation has been designed for the continuous treatment of polluted effluents combining a catalytic fixed-bed reactor (FBR) operating in up-flow and a continuous stirred tank reactor (CSTR). The CSTR with a maximum 1 L capacity collects the inlet effluent and a recycled treated stream coming from the catalytic fixed-bed reactor. The CSTR provides several advantages on the overall CWHPO process: (i) homogenization of the feed and recirculation streams, (ii) pre-oxidation of pollutants by wet hydrogen peroxide oxidation or even catalytic wet hydrogen peroxide oxidation if small traces of iron species from the catalyst bed were accumulated in the circuit loop, and (iii) recirculation of a liquid stream through the FBR, that intensifies the degradation process.

The agglomerated Fe₂O₃/SBA-15 catalyst is located inside of the tubular FBR (30 cm long and 2 cm i.d.). In the normal operating mode, the inlet wastewater effluent, which was diluted up to medium TOC concentration (0.22–2.2 g/L), with different hydrogen peroxide amounts are pumped to the CSTR with a flow rate \( Q_A \) of 0.25 L/h, while the flow rate \( Q_R \) of the internal circuit that connects the FBR and CSTR is set to 2.5 L/h with an auxiliary second pump. Typically, 5 g of the agglomerated crystalline hematite supported over a mesostructured SBA-15 silica material (Fe₂O₃/SBA-15) with a particle size of 2 mm was located inside the FBR. The temperature in the FBR \( T_R \) was changed between 120–160°C, whereas the temperature in the CSTR was always kept constant at 80°C. In addition, a constant air flow of 0.15 mL/min was supplied to

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**Figure 1** | Experimental set-up of intensified CWHPO plant.
pressurize the installation \( (P_O_2 = 2 \text{ bar}) \) and provide and extra source of oxygen to enhance the oxidation of pollutants. The total pressure of the system was modified depending on the temperature of the fixed bed reactor in order to ensure the same oxygen concentration in aqueous solution that flows through the catalyst bed. Outlet streams of the intensified CWHPO installation were taken from the bottom of the CSTR or at the exit of the FBR. In both cases, the liquid level sensor of the CSTR acted on the valves that release the treated effluent either at the bottom of the CSTR or after the FBR.

**Analytical methods**

The catalytic activity of the oxidation treatment was evaluated by monitoring several parameters in the outlet aqueous solution such as the reduction of the Total Organic Carbon (TOC), the Chemical Oxygen Demand (COD) and the Biological Oxygen Demand (BOD). The hydrogen peroxide conversion, pH and iron concentration leached from the catalyst were also monitored along the treatment. The TOC content of the solutions was analysed using a combustion/non dispersive infrared gas analyser model TOC-V Shimadzu. COD analyses were performed by digestion of solutions prepared by adding 2 mL of sample into commercially available kits that contain potassium dichromate, sulphuric acid and mercuric sulphate (Lovibond\textsuperscript{w}). The COD concentration was determined by a colorimetric method based on ISO 15705:2003-01 method. The \( H_2O_2 \) interferences in COD measurements were subtracted employing the following correlation Equation \( (\text{Kang et al. 1999}) \):

\[
\text{COD} = \text{COD}_m - [0.4706 \times \text{[H}_2\text{O}_2\text{]}]
\]  

(1)

Where \( \text{COD}_m \) is the value obtained with standard method and \( \text{[H}_2\text{O}_2\text{]} \) is the hydrogen peroxide concentration, both of them in mg/L. Biological Oxygen Demand (BOD\textsubscript{5}) tests were carried out with the Lovibond\textsuperscript{w} OxiDirect\textsuperscript{w} BOD meter, based on manometric respirometers that relate the oxygen uptake caused by the respiration of the microorganism with the change of pressure of the sealed respirometer for 5 days. The efficacy of the treatment was also discussed according to other reported parameters used in literature such as a biodegradability index calculated from the BOD\textsubscript{5}/COD ratio (Farré et al. 2008; Elmolla & Chaudhuri 2009) and the Average Oxidation State (AOS) calculated by means of Equation (2) that considers the TOC and COD concentration (Mantzavinos et al. 2000):

\[
\text{AOS} = 4 - 1.5 \times \frac{\text{COD}}{\text{TOC}}
\]  

(2)

AOS can vary between \( +4 \) for \( CO_2 \), the most oxidized carbon state, and \( -4 \) for \( CH_4 \), the most reduced carbon state. AOS is a useful parameter to estimate the oxidation degree in a complex wastewater. Hydrogen peroxide conversion was determined by iodometric titration. Iron content and other metallic species in the effluents were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis collected in a Varian VISTA AX system. Standard Methods were performed to characterize the inlet effluent. Such as, Total Suspended Solids using the 2540 D method, carbonates and bicarbonates by 2520 Standard Method, and different electrodes were used for pH, conductivity, nitrate, chloride and ammonium concentrations.

**RESULTS AND DISCUSSION**

**Petrochemical wastewater characterization**

The wastewater from a propylene oxide/styrene monomer and derivatives chemical production plants is characterized by a high strength of aromatic and polyol compounds and basic pH. It was also remarkable the negligible chloride concentration which is a key factor in the selection and cost of the equipments. This data enables the application of stainless steel reactors without risk of strong corrosion under acidic and oxidant conditions. The ratio between the biological and chemical oxygen demands (BOD\textsubscript{5}/COD) revealed poor biodegradability of the wastewater, whereas AOS value indicated the presence of organic compounds with low oxidation degree. Regarding the presence of metallic species, a significant concentration of molybdenum was detected due to molybdenum-containing catalysts are used in the propylene oxide production process. \textbf{Table 1} depicts the characterization results of the diluted
petrochemical wastewater that has been used for the study of the operating conditions of intensified CWHPO installation.

**Influence of the temperature and hydrogen peroxide concentration**

Preliminary studies of this installation demonstrated a positive effect of elevated recirculating flow rates with values of c.a. 10 times higher than the feeding flow rate for the treatment of phenolic aqueous solutions (Martínez et al. 2006; Pariente 2008). According to these previous results, in this work the recirculating flow rate was set to 2.5 L/h in order to provide a high weight hourly space velocity (WHSV) in the FBR that reduces mass transfer limitations, and the feed flow rate was set to 0.25 L/h in order to establish high residence times of the effluent in the overall pilot plant. The temperature of the catalytic fixed bed reactor and the amount of hydrogen peroxide used as oxidant for the treatment of petrochemical wastewater effluents of different concentrations were the variables studied in terms of the TOC reduction and the catalyst stability. Additionally, the BOD/COD ratio and the Average Oxidation State (AOS) value were also evaluated for the most favourable operating conditions.

Table 2 depicts the parameters monitored for the catalytic runs of the petrochemical wastewater diluted up to 1.1 g/L of TOC concentration. These parameters were TOC degradation, H$_2$O$_2$ conversion, pH and iron concentration in the outlet streams withdrawn on the CSTR and after FBR. The results of the samples taken after the FBR demonstrate the important role of the supported Fenton-like catalyst in this process with an increase of the TOC removal until c.a. 40 – 43%. It can be seen that the increase of the temperature from 120 to 160°C hardly improves the overall TOC degradation. In contrast, it is remarkable the enhancement of the hydrogen peroxide conversion as the temperature is increased, which can be responding to the partial oxidation of pollutants to more oxygenated by-products. Regards to the catalyst stability, the iron concentration in the outlet effluent is higher as the temperature is decreased. Several works have proven that the iron leaching of heterogeneous CWHPO catalysts is dramatically affected by the presence of low molecular weight carboxylic acids such as the oxalic acid (Zazo et al. 2006; Pariente 2008). So, the low iron leaching as temperature of FBR increases is probably attributed to the most effective degradation of these refractory acid by-products. On the other hand, the analysis of the effluents taken from the bottom of the CSTR indicates a lower TOC reduction with values ranging from 21 to 26% as a result of the dilution of the inlet effluent with the treated recirculating stream. Nevertheless, note also that part of TOC reduction can also be due to the thermal oxidation of the organic pollutants in the CSTR at 80°C and relatively high hydrogen peroxide concentrations.

Following, several catalytic runs were also conducted with different dosages of hydrogen peroxide in the inlet stream (7, 14 and 21 gH$_2$O$_2$/gTOC). Table 3 shows the TOC and oxidant conversions as well as the pH and the iron detected in the outlet effluent for the three hydrogen peroxide/TOC ratios at 160°C. An increase of the hydrogen peroxide concentration in the inlet effluent yields a significant enhancement of the degradation in both CSTR

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>TSS (mg/L)</td>
<td>&lt;0.9</td>
<td>Fe (mg/L)</td>
<td>0.05</td>
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<tr>
<td>[Cl$^-$] (mg/L)</td>
<td>&lt;1</td>
<td>Cu (mg/L)</td>
<td>0.40</td>
</tr>
<tr>
<td>[CO$_3^{2-}$] (mg/L)</td>
<td>576</td>
<td>Cu (mg/L)</td>
<td>0.03</td>
</tr>
<tr>
<td>[HCO$_3^-$] (mg/L)</td>
<td>&lt;0.5</td>
<td>Mg (mg/L)</td>
<td>0.03</td>
</tr>
<tr>
<td>pH</td>
<td>12.2</td>
<td>Mn (mg/L)</td>
<td>0.03</td>
</tr>
<tr>
<td>λ (mg/L)</td>
<td>3.14</td>
<td>Mo (mg/L)</td>
<td>7.00</td>
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<tr>
<td>[NO$_3^-$] (mg/L)</td>
<td>369</td>
<td>Na (mg/L)</td>
<td>825</td>
</tr>
<tr>
<td>[NH$_4^+$] (mg/L)</td>
<td>&lt;1</td>
<td>S (mg/L)</td>
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<td>Si (mg/L)</td>
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<td>Zn (mg/L)</td>
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<td>TOC (mg/L)</td>
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<td>BOD/COD</td>
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</tr>
<tr>
<td>AOS</td>
<td></td>
<td></td>
<td>−0.73</td>
</tr>
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Table 1 | Characterization data of the industrial petrochemical wastewater

Table 2 | Influence of the temperature in the fixed bed reactor for the catalytic wet hydrogen peroxide oxidation of a petrochemical wastewater. Operation conditions: $Q_a = 0.25$ L/h; $Q_e = 2.5$ L/h; $w_{rec} = 5$ g; $P_{rec} = 2$ bar; [TOC]$_0 = 1.1$ g/L; $[H_2O_2]_{rec} = 14$ gH$_2$O$_2$/gTOC

<table>
<thead>
<tr>
<th>T$_a$ (°C)</th>
<th>$X_{TOC}$ (%)</th>
<th>$X_{H_2O_2}$ (%)</th>
<th>pH</th>
<th>$X_{TOC}$ (%)</th>
<th>$X_{H_2O_2}$ (%)</th>
<th>Fe (mg/L)</th>
</tr>
</thead>
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<tr>
<td>120</td>
<td>22</td>
<td>21</td>
<td>2.8</td>
<td>3.2</td>
<td>40</td>
<td>56</td>
</tr>
<tr>
<td>140</td>
<td>21</td>
<td>26</td>
<td>3.3</td>
<td>0.8</td>
<td>42</td>
<td>74</td>
</tr>
<tr>
<td>160</td>
<td>26</td>
<td>27</td>
<td>3.9</td>
<td>0.3</td>
<td>43</td>
<td>90</td>
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</table>

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and FBR outlet effluents. Regarding the hydrogen peroxide concentration at the exit of the FBR, it can be seen a low variation on the oxidant conversion, which fluctuates between 80–90%, regardless of the oxidant dosage. In contrast, lower hydrogen peroxide conversions were found in the samples taken from the CSTR, as result of the oxidant fed through the inlet effluent. These results evidence the high activity of the iron catalyst located in the fixed bed reactor for the production of highly reactive hydroxyl radicals (HO•) that oxidize the polluted organic matter. The increase of the TOC degradation with the hydrogen peroxide concentration still maintains the possibility of enhancing the TOC mineralization at expenses of higher oxidant/TOC ratios in the inlet wastewater stream. Concerning the catalyst stability, it is observed that the treatment with higher hydrogen peroxide dosages yields lower amounts of iron leaching, achieving remarkable low iron concentrations into the outlet effluent below 4 mg/L.

Taking into account the catalytic runs carried out with different temperatures and hydrogen peroxide dosages, 160°C and 14 g H2O2/gTOC were considered the most favourable operation conditions. The highest temperature provided a low iron leaching of the catalyst and the intermediate oxidant concentration was good enough to achieve TOC degradation values higher than 40%. Profiles of TOC and H2O2 conversions, pH and iron concentration detected in the outlet FBR effluent along the time on stream are shown in Figure 2. These profiles indicate constant values of all the mentioned parameters once the steady-state was achieved until 8 hour. This fact is considered a good sign for the application of this intensified CWHPO process for the treatment of real wastewaters. Nevertheless, the complex composition of any wastewater could have a very different effect on the catalyst properties, hindering its application at pilot plant scale.

Table 3 | Influence of the hydrogen peroxide concentration in the inlet stream for the catalytic wet hydrogen peroxide oxidation of a petrochemical wastewater.

<table>
<thead>
<tr>
<th>[H2O2] (gH2O2/gTOC)</th>
<th>STR sample</th>
<th>FBR sample</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>XTOC (%)</td>
<td>XH2O2 (%)</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>17</td>
</tr>
<tr>
<td>14</td>
<td>26</td>
<td>27</td>
</tr>
<tr>
<td>21</td>
<td>33</td>
<td>14</td>
</tr>
</tbody>
</table>

Figure 2 | Catalytic activity and profiles in the best conditions: Qa = 0.25 L/h; Qe = 2.5 L/h; wcat = 5 g; P0 = 2 bar; Tn = 160°C; Ta = 80°C; [H2O2]0 = 14 g H2O2/gTOC. (a) TOC degradation, (b) H2O2 conversion, (c) pH and (d) iron leached out from the catalyst.
Influence of the petrochemical wastewater concentration

Regarding the previous study of the temperature and weight hydrogen peroxide/TOC ratio for the petrochemical wastewater with a TOC content of 1.1 g/L, 160°C and 14 gH₂O₂/gTOC, were maintained constant for the treatment of the wastewater with different dilution degrees which gives TOC loadings between 0.22 and 2.2 g/L. As seen in Table 4, TOC conversion decreases with increasing initial TOC concentration of the inlet wastewater stream. In contrast, the hydrogen peroxide conversion is 79, 90 and 92% for the runs performed at initial TOC concentrations of 0.22, 1.1 and 2.2 g/L, respectively. Concerning to the catalyst stability, the dissolution of iron into the liquid phase is strongly affected by the TOC loading. This seems to be in agreement with the theory reported in literature about a higher potential extraction of concentrated aqueous solutions that contains aromatic compounds, because these products are responsible of reductive-oxidative reactions over the iron sites of catalyst that promotes the iron dissolution in the liquid phase (Santos et al. 2005; Martínez et al. 2007).

A significant decrease of TOC conversion was evidenced when the inlet wastewater concentration was increased until 2.2 g/L, whereas for a more diluted wastewater stream (0.22 g/L) the TOC degradation reached up to 50%. The significant reduction of catalytic performance in terms of TOC conversion for wastewater streams with TOC loadings higher than 1.1 g/L indicates the actual limitation of this intensified CWHPO process for the treatment of concentrated effluents. Nevertheless, the optimization of operating conditions such as the decrease of the weight hourly space velocity, which means the increasing of the residence of the overall pilot plant, the increase of temperature in the CSTR or the increase of the hydrogen peroxide/TOC ratio are considered promising alternatives for the application of this intensified technology to more concentrated wastewater streams.

For the case of the wastewater stream diluted up to 1.1 g/L where temperature and weight hydrogen peroxide/TOC ratio were optimized, other parameters such as COD and BOD₃ were also measured. Table 5 summarizes the characterization data of the inlet and outlet samples taken after the FBR. It is clearly evidenced a reduction of the organic matter in the treated wastewater with lower values of COD, BOD and TOC. Looking at the BOD₃/COD ratio, the treated effluent showed a significant increase from 0.13 to 0.25, which evidences a more biodegradable effluent. Negatives values of AOS were determined for the inlet and treated streams, which indicates a low oxidation state of the organic pollutants present in the wastewater. However, after treatment this AOS increase from −0.73 to −0.14. From these results and the TOC reduction, it can be attested a low increase of the pollutants oxidation state with a noteworthy TOC mineralization. This indicates that the catalytic process was able to remove a significant fraction of organic pollutants until its total mineralization but other pollutants, either already present in the wastewater stream or result of the partial oxidation of original pollutants, seems to be quite refractory to be oxidized. Additionally, some of the remnant pollutants are more biodegradable, as can be deduced for the increase of the biodegradability.

CONCLUSIONS

The intensified wet hydrogen peroxide oxidation heterogeneously catalyzed by agglomerated Fe₂O₃/SBA-15 catalyst is shown as an interesting alternative for the treatment

<table>
<thead>
<tr>
<th>[TOC] (g/L)</th>
<th>X_TOC (%)</th>
<th>X₉₅O₂ (%)</th>
<th>pH</th>
<th>Fe (mg/L)</th>
</tr>
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<tbody>
<tr>
<td>0.22</td>
<td>55</td>
<td>79</td>
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<td>0.1</td>
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<td>1.1</td>
<td>43</td>
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<td>2.8</td>
<td>0.8</td>
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<tr>
<td>2.2</td>
<td>10</td>
<td>92</td>
<td>3.7</td>
<td>9.6</td>
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</table>

Table 5 | Wastewater characterization before and after the CWHPO process

<table>
<thead>
<tr>
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<th>Inlet effluent</th>
<th>Outlet effluent</th>
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<tbody>
<tr>
<td>pH</td>
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<td>2.8</td>
</tr>
<tr>
<td>COD (mg/L)</td>
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<td>1,732</td>
</tr>
<tr>
<td>BOD₃ (mg/L)</td>
<td>442</td>
<td>433</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
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<td>−0.14</td>
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of a petrochemical wastewater. TOC reduction of 43% and low deactivation by iron leaching (<1 mg/L) were obtained at 160°C and 14 grams of H₂O₂ per gram of TOC for the treatment of a diluted wastewater with a medium TOC concentration of 1.1 mg/L. Moreover, the analysis of the outlet effluent in the most favourable reaction conditions indicates not only a significant TOC reduction (45%), but also an increase in the biodegradability with a BOD₅/COD ratio of 0.25 as compared to the initial 0.13. However, the compounds still present in the treated effluent seem to be quite resistant to the oxidation process with a relatively low average oxidation state (~0.14). The catalytic performance of intensified CWHPO process and catalyst stability was drastically affected for the treatment of wastewater streams with TOC concentrations higher than 1.1 g/L. Further research is being addressed to the search of better operating conditions that allows the treatment of more concentrated streams by intensified CWHPO processes.

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