Heterogeneous catalytic wet peroxide oxidation systems for the treatment of an industrial pharmaceutical wastewater

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ABSTRACT

The aim of this work was to assess the treatment of wastewater coming from a pharmaceutical plant through a continuous heterogeneous catalytic wet peroxide oxidation (CWPO) process using an Fe_2O_3/SBA-15 nanocomposite catalyst. This catalyst was preliminary tested in a batch stirred tank reactor (STR), to elucidate the influence of significant parameters on the oxidation system, such as temperature, initial oxidant concentration and initial pH of the reaction medium. In that case, a temperature of 80 °C using an initial oxidant concentration corresponding to twice the theoretical stoichiometric amount for complete carbon depletion and initial pH of ca. 3 allow TOC degradation of around 50% after 200 min of contact time. Thereafter, the powder catalyst was extruded with bentonite to prepare pellets that could be used in a fixed bed reactor (FBR). Results in the up-flow FBR indicate that the catalyst shows high activity in terms of TOC mineralization (ca. 60% under steady-state conditions), with an excellent use of the oxidant and high stability of the supported iron species. The activity of the catalyst is kept constant, at least, for 55 h of reaction. Furthermore, the BOD_5/COD ratio is increased from 0.20 to 0.30, whereas the average oxidation stage (AOS) changed from 0.70 to 2.35. These two parameters show a high oxidation degree of organic compounds in the outlet effluent, which enhances its biodegradability, and favours the possibility of a subsequent coupling with a conventional biological treatment.

1. Introduction

The treatment of pharmaceutical wastewaters has emerged as an important concern during the last decade. The effective removal of substances included in pharmaceutical residual effluents is a challenging task due to the wide variety of chemicals produced in drug manufacturing plants, which lead to wastewaters of variable compositions (Zwiener and Frimmel, 2000). Likewise, in most cases, the substances related to the pharmaceutical industry are resistant to biological degradation. Therefore, chemical treatments or pre-treatments to increase the biological depuration of effluents are necessary. Among these chemical processes, advanced oxidation processes (AOPs) have been successfully used for the removal or degradation of recalcitrant pollutants present in wastewater from different industries (Silva et al., 2004; Schrank et al., 2005; Klavarioti et al., 2009). These processes involve the generation of hydroxyl radicals (•OH) with high oxidative power (Plant and Jeff, 1994). Among AOPs, Fenton's reagent (Fenton, 1894) has emerged as an interesting alternative for the treatment of dissolved organic pollutants in wastewater streams. This homogeneous catalytic method is based on the generation of powerful •OH radicals from hydrogen peroxide in the presence of a metallic ion,

commonly Fe(II), or other low valence transition metals, Fe(III), Cu(II) or Mn(II), dissolved in the aqueous medium. The generation of hydroxyl radicals can be enhanced by heating or using UV irradiation. However, the limited range of the pH (3–4) in which the reaction proceeds and the need for recovery of homogeneous catalyst to comply with European environmental regulations (European Economic Community, EEC, 1982) are the major drawbacks of this technology. In order to avoid the continuous loss of catalyst and the need for removing the iron after treatment, a growing research effort focused on the immobilization of transition metals (especially iron species) over different supports is already being undertaken by different research groups (Centi et al., 2000; Ovejero et al., 2001; Guélou et al., 2003; Yuranova et al., 2004; Liou et al., 2005). In line with these works, our research group has recently published a solid catalyst consisting of a crystalline Fe_2O_3/SBA-15 nanocomposite which exhibits a high degradation rate for the mineralization of phenolic aqueous solutions in a wide range of pH, using moderate amounts of oxidant and with a remarkable stability of the iron oxides supported on the silica support (Melero et al., 2007).

In addition to basic studies using target compounds as models, Fenton-like reactions have been efficiently used as oxidation processes for the treatment of real industrial wastewaters (Pérez et al., 2002a; Pérez et al., 2002b;Ormad et al., 2006;Kurt et al., 2006; Bautista et al., 2008), including pharmaceutical ones (Zgajnar and Zagorc-Konkan, 2005; Tekin et al., 2006) resulting in a significant reduction of toxicity, improvement of biodegradability, and colour and odour removal. Nevertheless, works described in the literature have used homogeneous Fenton reactions, maintaining the acidic medium and post-treatment steps to remove the iron species.

A step forward is carried out in this work using an Fe_2O_3/SBA-15 material as a Fenton-like heterogeneous catalyst for the treatment of a pharmaceutical wastewater by catalytic wet oxidation in the presence of hydrogen peroxide (CWPO), in a continuous up-flow fixed bed reactor (FBR). Continuous Fenton catalytic systems have been poorly dealt with in the literature in comparison to, for instance, catalytic wet air oxidation processes using oxygen from air as oxidant (Stüber et al., 2001; Álvarez et al., 2002a,b; Santos et al., 2005). Wastewater feed flow rate, hydrogen peroxide concentration and initial pH of the inlet stream effect were widely studied in order to determine the optimal reaction conditions that yielded the highest TOC degradation, as well as catalyst stability. To the best of our knowledge, the work reported here is the first to deal with the treatment of a real industrial wastewater by CWPO process over a heterogeneous catalyst in an FBR.

2. Methods

2.1. Pharmaceutical wastewater characterization

The wastewater was obtained from a large scale drug and fine chemical manufacturing industrial plant located in the south of Madrid, Spain. This industry is focused on the synthesis of specific drugs for cardiovascular and venous diseases, as well

as diabetes. Table 1 shows the most relevant characteristics and composition of the pharmaceutical wastewater. The wastewater presents a variable composition in time that makes it hard to list the organic compounds present in the stream. The BOD_5/COD ratio reveals poor biodegradability of the raw wastewater, whereas the average oxidation state (AOS, Scott and Ollis, 1995; Mantzavinos et al., 2000) indicates the presence of organic compounds with moderate oxidation degree. At this point, it should be indicated that the wastewater selected for this study is currently treated by a conventional homogeneous Fenton process with high excess of oxidant and a considerable concentration of homogeneous iron and copper salts. This homogeneous treatment exhibits a high organic degradation and complies with strict environmental regulations but it has the above-mentioned drawbacks.

2.2. Catalyst preparation and characterization

Iron oxide supported into a SBA-15 mesostructured material was prepared by co-condensation of iron ($FeCl_3 \cdot 6H_2O$; Aldrich) and silica (tetraethoxysilicate, TEOS; Aldrich) sources under acidic conditions and templated with Pluronic 123 as described elsewhere (Martínez et al., 2002). The procedure described in the literature was slightly modified, changing the ageing pH up to 3.5 by addition of an appropriate amount of ammonia aqueous solution, in order to promote the formation and precipitation of iron oxo-hydroxydes particles (Lázár et al., 2004). The resultant solution was aged at 110 °C for 24 h under static conditions. The solid product was recovered by filtration, and calcined in air at 550 °C for 5 h, removing the template and promoting the crystallization of iron oxides.

For the preparation of the catalytic packed bed, Fe_2O_3/SBA-15 nanocomposite material was extruded by blending the fresh powder catalyst (75 wt%) with sodium bentonite (25 wt%) and synthetic methylcellulose polymer which acts as binder in the extrusion process. All the components were kneaded under high shear conditions until a homogeneous paste was achieved a adding controlled dosage of deionized water. Thereafter, the solid paste was placed in a damp atmosphere, which provides the proper plasticity to be easily extrudable as well as the required cohesive properties

Table 1 – Main features of the industrial pharmaceutical wastewater.

Parameter	Value
pH	5.6
COD (mg O_2/L)	1901
TOC (mg/L)	860
BOD_5 (mg O_2/L)	381
$[CO_3^{2-}]$ (mg/L)	0
$[HCO_3^-]$ (mg/L)	112
$[NO_3^-]$ (mg/L)	500
$[NH_4^+]$ (mg/L)	4.8
$[Cl^-]$ (mg/L)	3380
Suspended solids (mg/L)	40.6
BOD_5/COD	0.20
Average oxidation state (AOS)	0.70

(González-Velasco et al., 1999). The paste was then passed through a 5 mm circular die using a ram extruder. The shaped-rod product was dried for 3 days in a controlled temperature and humidity chamber with temperature and relative humidity ranges of 20–40 °C and 70–10%, respectively. After that, conformed catalyst was calcined at 650 °C in air for 2 h, using a slow ramp of temperature to remove water gradually, burning off the organic content and enhancing the mechanical strength of the calcined extrudates by sintering of the inorganic binder (Martínez et al., 2007). The final Fe_2O_3/SBA-15 pellets were obtained by crushing and sieving the extruded material to particle sizes ranging from 1.0 to 1.6 mm. Table 2 summarizes the most relevant properties of the extruded material, in comparison to the raw powder Fe_2O_3/SBA-15 sample.

According to previous works (Lázár et al., 2004; Martínez et al., 2005) the powder catalyst can be described as a composite material that contains different iron oxides particles (mainly crystalline hematite) embedded on a meso-structured SBA-15 matrix, and a small amount of ionic Fe^{3+} species included in the framework by isomorphous substitution of Si ions. Average particle diameter is 14.4 μm. The iron oxide particles are presented in a wide distribution of sizes (30–3000 nm). The total iron content was around 19 wt%, and the support exhibits a BET surface area slightly lower than that usually found for pure SBA-15 (ca. 495 m^2/g and ca. 800 m^2/g, respectively) and a narrow pore diameter distribution centred in 79 Å. On the other hand, extruded catalyst maintains the presence of crystalline hematite entities as well as mesoscopic order and narrow pore diameter distribution typical of the SBA-15 topology. Nevertheless, BET surface area decreases significantly in the extruded materials, as a result of the presence of bentonite and sintering processes during the calcination step of the extrusion process. Likewise, the existence of bentonite produces a slight solid dilution of iron content in the extruded material.

2.3. Preliminary catalytic runs performed in a discontinuous stirred tank reactor (STR)

Preliminary catalytic wet peroxide oxidation experiments were performed in a 100 mL glass autoclave reactor, with a total reaction volume of 75 mL, and mechanically stirred at 350 rpm. An appropriate amount of catalyst suspended in the wastewater (0.6 g/L) was placed into the glass reactor. Then,

the system was pressurized up to 7 bar with air and heated to the selected reaction temperature. When the required temperature was achieved, the corresponding amount of hydrogen peroxide was added to the reactor, and the reaction started. Total reaction time was fixed at 4 h. Samples were withdrawn every 30 min and filtered through a 0.22 μm nylon filter.

2.4. Catalytic runs performed in a continuous up-flow fixed bed reactor (FBR)

The continuous CWPO experiments were conducted in an up-flow FBR working under atmospheric pressure. The FBR consists of a jacketed glassware tube of 1.2 cm inner diameter and 15 cm length. A catalyst mass (w_{cat}) of 2.9 g was placed in the catalytic packed bed between two beds of spherical inert glass particles. An appropriate mixture of wastewater and hydrogen peroxide was pumped to the packed bed reactor by means of a Gilson 10SC HPLC pump operating at variable flow. The temperature of the system on the upper part of the bed was controlled at 80 °C using an external recirculating heating bath with a stream of silicon oil through the jacket of the glass reactor. Time zero is considered to be when the feed flow reaches the top of the catalytic bed. The residence time for the liquid phase in the packed bed reactor was calculated following the procedure previously described in the literature taking into account the bed porosity (ε) and the liquid hold up (h_L) of the packed bed (Martínez et al., 2007).

2.5. Analytical techniques for water samples and reaction parameters

Total organic carbon (TOC) content of the samples was analysed using a combustion/non-dispersive infrared gas analyser model TOC-V from Shimadzu. Residual hydrogen peroxide in the samples was measured by iodometric titration. Finally, iron content in the filtered solution after reaction was measured by ICP-AES analysis collected in a Varian Vista AX spectrometer in order to determinate the leaching degree from the catalyst within the effluent. Chemical oxygen demand (COD) was analysed by a standard method using potassium dichromate as oxidizing agent (APHA, 1998). Hydrogen peroxide interferes in COD measurement overestimating the results obtained by the method. COD value

Table 2 – Physicochemical properties of the materials.

	Average particle size (μm)	S_{BET} (m^2/g)[b]	Pore diameter d_p (nm)[b]	Iron content (wt%)[c]	Iron oxide as hematite[d]
Fe_2O_3/SBA-15 (powder)	14.4[a]	495	7.9	19	Yes
Bentonite (powder)	6.2[a]	119	7.2	2	–
Extruded Fe_2O_3/SBA-15	1000–1600[e]	264	8.1	14	Yes

a Analysed by laser scattering technique.
b Determined by N_2 adsorption isotherms at 77 K.
c Detected by ICP-AES.
d Detected by X-ray diffraction.
e Sieving.

eliminating hydrogen peroxide interference can be obtained by Eq. (1) (Kang et al., 1999):

$$COD = COD_m - 0.4706[H_2O_2] \qquad (1)$$

where COD_m is the value obtained with the standard method and $[H_2O_2]$ is the hydrogen peroxide concentration detected in the measured sample by iodometric titration, all of them expressed in milligrams per litre. Finally, biochemical oxygen demand (BOD) was defined as the amount of oxygen consumed by the sample over 5 days at 20 °C, according to the appropriate standard method (APHA, 1998), in milligrams of O_2 per litre. The performance of the reaction was studied following the parameters described by Eqs. (2)–(6).

$$\text{TOC conversion, } X_{TOC}(\%) = \frac{[TOC]_{inlet} - [TOC]_{outlet}}{[TOC]_{inlet}} \times 100 \qquad (2)$$

$$\text{Oxidant consumption, } X_{H_2O_2}(\%) = \frac{[H_2O_2]_{inlet} - [H_2O_2]_{outlet}}{[H_2O_2]_{inlet}} \times 100 \qquad (3)$$

$$\text{Efficiency of the oxidant, } \eta = \frac{\text{Theoretical consumption of } H_2O_2}{\text{Real consumption of } H_2O_2} \qquad (4)$$

$$\text{Biodegradability} = \frac{BOD_5}{COD} \qquad (5)$$

$$\text{Average oxidation state (AOS)} = 4 - 1.5 \times \frac{COD}{TOC} \qquad (6)$$

3. Results and discussion

3.1. Preliminary CWPO experiments in a discontinuous STR

Experiments in the discontinuous tank reactor were performed in order to assess the influence of three significant variables (temperature, initial pH and hydrogen peroxide concentration) on the activity and stability of the catalyst. The activity was evaluated in terms of TOC conversion, whereas stability was measured as iron leached from the catalyst after a reaction test.

Hydrogen peroxide concentration has a critical influence on the performance of the Fenton systems (Neyens et al., 2003; Pera-Titus et al., 2004). For a wastewater with unknown composition, the stoichiometric amount of hydrogen peroxide for a theoretical mineralization of organic carbon can be obtained by the following reaction:

$$C + 2H_2O_2 \rightarrow CO_2 + 2H_2O \qquad (7)$$

A molar ratio H_2O_2/C of 2, equivalent to a 5.6 mass ratio, is necessary for complete carbon depletion following the stoichiometry of the reaction. Taking into account the TOC content in the pharmaceutical wastewater (860 mg/L), the stoichiometric hydrogen peroxide concentration for its theoretical complete oxidation is ca. 4820 mg/L. Since wastewater might include other compounds susceptible to being oxidized by hydrogen peroxide, the stoichiometric H_2O_2/C mass ratio
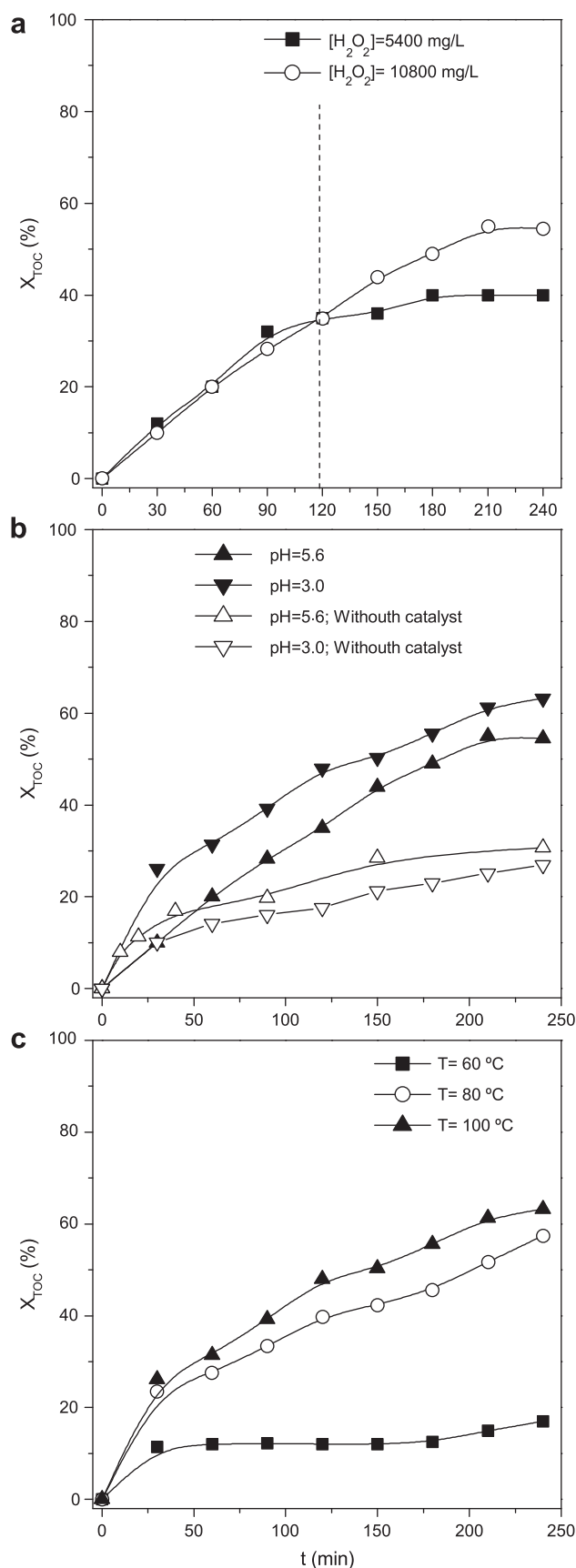

Fig. 1 – Catalytic runs in the STR(a) Influence of hydrogen peroxide concentration. T = 100 °C; pH$_0$ = 5.6; [catalyst] = 0.6 g/L.(b)Influence of initial pH. T = 100 °C; [H$_2$O$_2$]$_0$ = 10,800 mg/L; [catalyst] = 0.6 g/L (c) Influence of reaction temperature. pH$_o$ = 3; [H$_2$O$_2$]$_0$ = 10,800 mg/L; [catalyst] = 0.6 g/L.

has been slightly increased up to 7. Reactions tests at two different initial hydrogen peroxide concentrations (5400 mg/L and 10,800 mg/L, with H_2O_2/C mass ratios of 7 and 14, respectively) were performed obtaining the TOC conversion profiles depicted in Fig. 1a. TOC conversions are very close in both cases during the first 120 min of reaction. After this time, the benefits of an excess of oxidant are clearly relevant, achieving ca. 55% of TOC degradation, in comparison to that of ca. 40% obtained using 5400 mg/L, which is related to a complete conversion of the hydrogen peroxide for the latter. Negligible TOC conversion was achieved in the absence of oxidant.

On the other hand, the pH of the reaction medium also has a critical influence in Fenton-like reactions (Melero et al., 2007). A pH between 3 and 4 is optimum for these types of advanced oxidation processes. In order to evaluate the influence of the initial pH of the aqueous solution in the STR, additional experiments were performed with acidified pharmaceutical wastewater up to pH values of ca. 3, adding the appropriate amount of a sulphuric acid solution (0.1 N). Fig. 1b shows TOC conversion profiles for reaction tests carried out with an initial hydrogen peroxide concentration of 10,800 mg/L and initial pH of 3 and 5.6, the later corresponding to the natural pH of the wastewater. The results reveal a slight increase in the degradation rate with the decrease of the initial pH of the solution which is more accentuated in the initial stages of the reaction. Note that a gradual decrease of the aqueous solution pH up to ca. 2.6 is observed for both catalytic runs.

The effect of the reaction temperature in the activity of the heterogeneous catalytic system was also studied. Fig. 1c shows TOC conversion profiles of reactions performed at 60, 80 and 100 °C, using 10,800 mg/L of hydrogen peroxide and an initial pH of ca. 3. Results reveal that a temperature of 80 °C is necessary to obtain an appreciable TOC degradation during the process. An increase of temperature from 80 to 100 °C produces only a slight increase in TOC conversion, especially at final reaction time (ca. 8%).

It is remarkable that in the reaction tests performed in this first part of the study, the iron detected within the reaction medium after 240 min of reaction hardly reaches 6 mg/L, which corresponds to the loss of ca. 6% of iron initially contained by the solid catalyst. Particularly, the catalytic run carried out at 80 °C, initial pH of 3 and initial hydrogen peroxide concentration of 10,800 mg/L allows a TOC conversion of ca. 58% after 240 min, accompanied by an iron leaching degree of 4.8%, which corresponds to a concentration of iron in the reaction medium of ca. 4.8 mg/L.

Finally two blank reactions were performed in the absence of catalyst and two different pH values (Fig. 1b). In both cases, the benefits of the catalyst are clearly evidenced, showing a significant enhancement of the TOC degradation rate.

3.2. Oxidation reactions of the real wastewater in a continuous fixed bed reactor

Some of the reaction conditions fixed in this part of the work were selected according to the results previously obtained in the STR, as well as the optimized conditions in the same FBR system using phenol as the model compound (Martínez et al., 2007). Thus, all the catalytic runs were conducted in the FBR ($L = 15$ cm and $d_i = 1.2$ cm) at 80 °C, under atmospheric pressure, and using 2.9 g of catalyst. Likewise, an aqueous solution of the wastewater (860 mg/L of TOC content) and hydrogen peroxide (10,800 mg/L, equivalent to twice the stoichiometric amount for the theoretical complete mineralization of the TOC content) acidified up to pH 3 was used as inlet stream. In the following sections, the influence of other operation variables will be discussed.

3.2.1. Influence of the feed flow rate
In order to evaluate the influence of residence time on organic degradation, three experiments were performed using feed flow rates of 0.25, 0.50 and 1.00 mL/min. These flows provide residence times for the liquid phase of 3.79, 1.90 and 0.95 min, respectively (Martínez et al., 2007). TOC and hydrogen peroxide conversion profiles along with the time on stream are depicted in Fig. 2a,b.
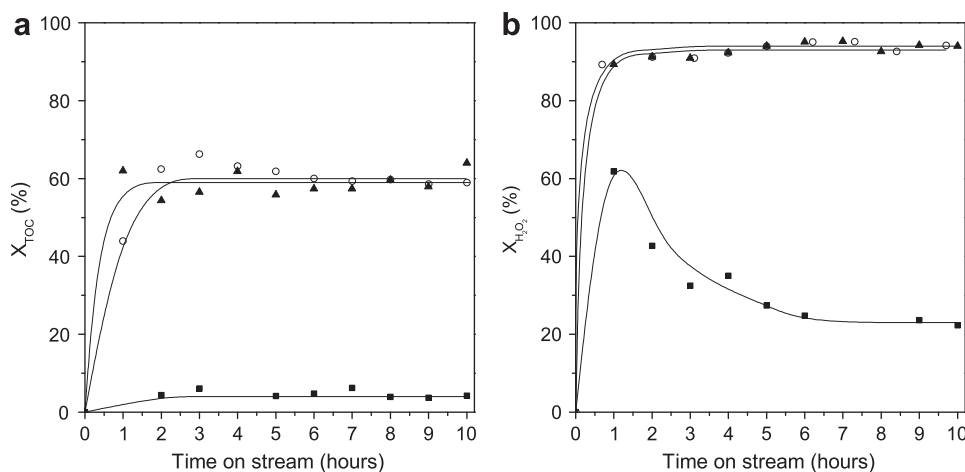

Fig. 2 – Catalytic runs in the FBR. Influence of the residence time/feed flow rate on the TOC (a) and hydrogen peroxide (b) conversions with time on stream. Reaction conditions: feed flow rate (Q_{FEED}) ■ 1 mL/min; ○ 0.5 mL/min; ▲ 0.25 mL/min; T = 80 °C; w_{CAT} = 2.9 g; $[H_2O_2]_{inlet}$ = 10,800 mg/L; pH_0 = 3.
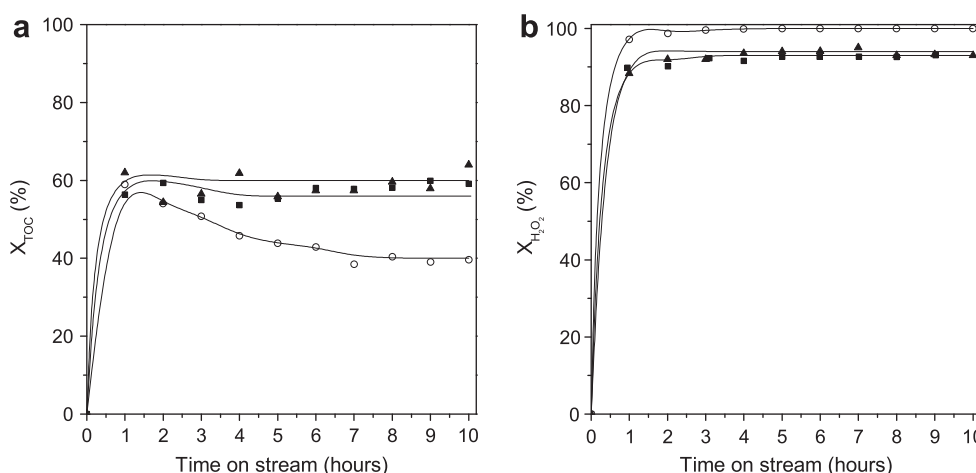
Fig. 3 – Catalytic runs in the FBR: influence of hydrogen peroxide concentration in the inlet effluent. TOC (a) and hydrogen peroxide (b) conversions with time on stream. Reaction conditions: $[H_2O_2]_{inlet}$ ■ 16,200 mg/L; ▲ 10800 mg/L; ○ 5400 mg/L; $T = 80\,°C$; $Q_{FEED} = 0.25$ mL/min; $w_{CAT} = 2.9$ g; $pH_0 = 3$.

An important effect can be seen when the feed flow rate is increased from 0.5 to 1 mL/min, (changing the liquid phase residence time from 1.90 to 0.95 min). A drastic decrease in the TOC removal, almost inhibiting the oxidation process, is achieved with a feed flow rate of 1 mL/min. On the other hand, Fig. 2b shows that an increase in residence time not only produces an enhancement of the TOC conversion, but also an important increase in the hydrogen peroxide conversion, up to 90%. Likewise, comparison between oxidant efficiencies reveals a very low value ($\eta = 0.08$) for the higher feed flow rate, as compared to that obtained when a feed flow of 0.5 mL/min is employed ($\eta = 0.25$). Summarizing, a feed flow of 1 mL/min provides a low residence time which is not able to promote efficient organic degradation and as a result the oxidant disappearance is mainly related to thermal decomposition. In contrast, the oxidant efficiency increases up to 0.25 when the feed flow rate is decreased to 0.5 mL/min, indicating that the oxidant is used efficiently for the generation of hydroxyl radicals, enhancing the activity of the heterogeneous catalytic system. Lowering the feed flow rate to 0.25 mL/min does not promote any improvement in the catalyst performance, obtaining similar catalytic results in terms of organic depletion (TOC conversion ca. 60%) and oxidant efficiency (ca. 0.25). It seems that there is a maximum TOC conversion (ca. 60%) and higher residence times are not enough to degrade refractory by-products formed during the organic depletion.

3.2.2. Influence of hydrogen peroxide concentration in the inlet stream

In the preliminary experiments carried out in the STR, the initial hydrogen peroxide concentration exhibited a high influence on the TOC degradation obtained after 240 min of reaction time. As the reaction mechanism could be different in batch and fixed bed reactors, due to the different catalyst–liquid ratio and contact (Bergault et al., 1997), the study of the effect of the initial hydrogen peroxide concentration in the inlet stream has also been considered for the FBR. Fig. 3 shows the catalytic results in terms of TOC and hydrogen peroxide

conversions using oxidant concentrations in the inlet stream of 5400, 10,800 and 16,200 mg/L, corresponding to twice and three times the stoichiometric loading, respectively.

A stoichiometric amount of oxidant yields a TOC degradation of around 40% under steady-state conditions. A hydrogen peroxide concentration twice the stoichiometric amount (10,800 mg/L) promotes an enhancement of the catalytic activity, allowing a steady TOC degradation value of ca. 60%. A further increase in the oxidant loading does not enhance the TOC degradation.

As has been mentioned previously, an important point in CWPO processes is the efficiency in the use of the oxidant. The oxidant efficiency parameter (η) decreases gradually with increasing hydrogen peroxide loading in the feed (Table 3). But whereas this value hardly varies when the initial oxidant concentration is changed from 5400 mg/L to 10,800 mg/L (0.33 and 0.26, respectively), there is an outstanding decrease when the hydrogen peroxide loading is up to 16,400 mg/L ($\eta = 0.18$). These catalytic results indicate that the use of an initial oxidant concentration twice the stoichiometric amount allows the obtaining of high organic degradation with a reasonable use of hydrogen peroxide. Upper oxidant

Table 3 – Influence of different operation variables for the treatment of a pharmaceutical wastewater (steady-state values).

Q_{FEED} (mL/min)	$[H_2O_2]_{inlet}$ (mg/L)	X_{TOC} (%)	$X_{H_2O_2}$ (%)	$[Fe]_{leaching}$ (mg/L)	η
1	10800	4	22	<0.05	0.08
0.5		58	94	<0.05	0.25
0.25		60	94	< 0.05	0.26
0.25	16200	61	94	<0.05	0.18
	10800	60	94	<0.05	0.26
	5400	40	100	< 0.05	0.33

Operation conditions: $w_{CAT} = 2.9$ g; $[TOC]_0 = 860$ mg/L; $T = 80\,°C$; $pH_{inlet} = 3$.

loadings in the feed stream do not improve the TOC degradation, yielding a worse use of the hydrogen peroxide. Nevertheless, in all cases, the efficiency is far from the unit value (which means maximum efficiency in the use of the oxidant) which indicates that not all the oxidant is efficiently used for TOC mineralization due to the formation of intermediate compounds more refractory to be oxidized or even scavenging reactions of the hydroxyl radicals.

Summarizing, Table 3 shows TOC and hydrogen peroxide conversions as well as oxidant efficiency and iron concentration in the outlet effluent under steady-state conditions for the different feed flow rates and oxidant loadings studied. As discussed earlier, a feed flow rate up to 0.5 mL/min and an oxidant loading twice the stoichiometric amount for complete carbon depletion enhance the TOC conversion and the efficient use of the oxidant. Likewise, the iron species concentration in the outlet aqueous solution was in all the cases below the detection limit of the ICP-AES (0.05 mg/L). This data indicates a high stability of the iron species supported over mesostructured material under the described reaction conditions. Another important point is the hydrogen peroxide conversion, which is a crucial parameter for a possible application in coupling oxidation–biological treatments. Under the optimized conditions of this work, oxidant conversions close to 100% in the outlet stream are achieved, making integration with a biological system possible.

3.2.3.   Long-term reaction

For an industrial application of this oxidation system it is crucial that the catalyst keeps its activity for long-term reactions. Fe_2O_3/SBA-15 extruded catalyst has shown high activity and extreme stability of the supported iron species in all the catalytic runs discussed above. However, all the reactions were finished after 10 h of time on stream. In order to determine the feasibility of the catalyst for long-term continuous treatments, an additional experiment was performed under the best reaction conditions ($w_{CAT} = 2.9$ g; $T = 80\ °C$; $Q_{FEED} = 0.25$ mL/min; $[H_2O_2]_{inlet} = 10{,}800$ mg/L; $pH_{inlet} = 3$), enlarging the time on stream to 55 h, giving the catalytic results shown in Fig. 4.

A slight decrease in the TOC conversion is observed after 20 h of time on stream, which is accompanied by a parallel decrease in the hydrogen peroxide consumption. According to previous results published with this catalyst in the degradation of phenolic aqueous solutions, the nature and environment of the iron active species might be modified during the treatment (Martínez al., 2007). However, the loss of activity observed with this industrial wastewater is less stressed than that previously observed with the same catalyst for the degradation of phenolic aqueous solutions. Hence, although the deactivation of the Fe_2O_3/SBA-15 catalyst could be due to changes in the iron species toward less active ones (Kong et al., 1998; Martínez et al., 2007), these iron environment changes seem to be dramatically influenced by the features of inlet effluent. Nevertheless, it can be considered that the catalyst keeps an almost constant activity after 55 h on stream in the range of 50–60% TOC conversion, showing a high stability of iron species, and the iron concentration in the outlet effluent being almost negligible. Likewise, the catalyst particles did not grind during the process.
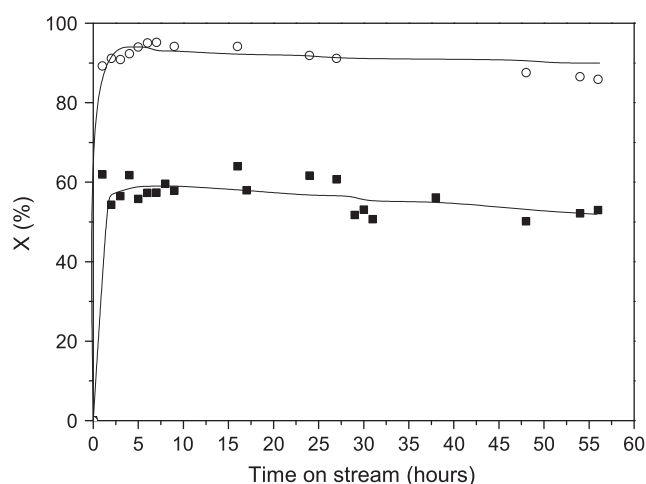

Fig. 4 – Catalytic runs in the FBR: long-term reaction. TOC (■) and hydrogen peroxide (○) conversion with time on stream under selected conditions: $T = 80\ °C$; $w_{CAT} = 2.9$ g; $[H_2O_2]_{inlet} = 10800$ mg/L; $pH_0 = 3$; $Q_{FEED} = 0.25$ mL/min.

3.2.4.   Characterization of the outlet effluent

In the final stage of the work, the exhaustive characterization of the outlet stream was carried out, with the results shown in Table 4. As result of the oxidation process, a reduction in the amount of organic matter can be clearly observed. COD removal attained in the system is about 81%. Interestingly, it can be seen that the chloride amount increases after the treatment. The pharmaceutical wastewater could contain chlorinated organic compounds that can be degraded during the Fenton-like oxidation, releasing chloride ions into the reaction medium (Gimeno et al., 2005). An outstanding increase in biodegradability (in terms of BOD_5/COD ratio) is also obtained after the treatment. This fact, as well as the increase in the AOS parameter, indicates that some of the wastewater components have been transformed into partially oxidized compounds, which are generally more biodegradable (Contreras et al., 2003). Summarizing, the treatment of the pharmaceutical wastewater over Fe_2O_3/SBA-15 heterogeneous catalyst in a continuous up-flow fixed bed reactor results in a significant reduction of organic matter, accompanied by an interesting enhancement of its biodegradability. It should be pointed out that these results were obtained using a moderate loading of hydrogen peroxide and with a high stability of iron species.

Table 4 – Pharmaceutical wastewater characterization after CWPO treatment.

Parameter	Inlet stream	Outlet stream	Reduction (%)	$\Delta_{parameter}$
COD (mgO_2/L)	1901	360	81	–
TOC (mg/L)	860	354	59	–
BOD_5 (mgO_2/L)	381	109	71	–
$[Cl^-]$ (mg/L)	3380	7050	–	+3670
BOD_5/COD	0.20	0.30	–	+0.1
AOS	0.70	2.35	–	+1.65

Finally, the results obtained with the FBR reactor under steady-state conditions are comparable to those achieved with conventional treatment of the wastewater in the pharmaceutical plant. In that case, a homogeneous and continuous Fenton-like system is employed, with temperatures ranging from 70 to 80 °C, hydrogen peroxide concentrations between 7000 and 12,000 mg/L, initial pH of ca. 3 and a homogeneous catalyst consisting of a mixture of Fe, Cu and Mn salts in concentration of 100–110 mg/L. Average TOC, COD and BOD_5 reductions of 70, 75 and 65% can be obtained with that homogeneous system, respectively. The FBR reactor under study achieves a TOC mineralization of 55–60%, whereas COD and BOD_5 reduction are around 80 and 70%, respectively. Furthermore, with our system sludge production, as well as additional steps for metal catalyst recovering, is avoided due to the high stability of iron species in the heterogeneous catalyst.

4. Conclusions

The Fe_2O_3/SBA-15 extruded catalyst exhibits high efficiency in the treatment of pharmaceutical wastewaters by catalytic wet peroxidation in a continuous fixed bed reactor. The high activity in terms of TOC mineralization and COD reduction is accompanied by a remarkable stability of the supported iron species. The catalytic assay up to 55 h on stream in an FBR allows stable steady TOC degradation values between 50 and 60% with an efficient use of the oxidant. Moreover, a remarkable enhancement in the biodegradability of the outlet effluent was achieved. BOD_5/COD ratio increased from 0.20 to 0.30, whereas the AOS rose from 0.70 to 2.35. The enhancement of both parameters makes the wastewater more biodegradable and suitable for being treated by a conventional biological depuration system.

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