1 HETEROGENEOUS CATALYTIC WET PEROXIDE OXIDATION

2 SYSTEMS FOR THE TREATMENT OF AN INDUSTRIAL

3 PHARMACEUTICAL WASTEWATER

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ABSTRACT

The aim of this work was to assess the treatment of a wastewater coming from a pharmaceutical plant through a continuous heterogeneous catalytic wet peroxide oxidation (CWPO) process using a 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 80ºC using an initial oxidant concentration corresponding to twice the theoretical stoichiometric amount for a complete carbon depletion and initial pH of ca. 3 allow obtaining TOC degradation around 50% after 200 minutes 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 hours of reaction. Furthermore, BOD_5/COD ratio is increased from 0.20 up 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 of cases, the substances related to the pharmaceutical industry are resistant to the biological degradation. Therefore, chemical treatments or pre-treatments to increase the effluent for the biological depuration 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 coming from different industries (Silva et al., 2004; Schrank et al., 2005; Klavarioti et al., 2009). These processes involve the generation of hydroxyl radicals ($^\bullet$HO) 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 $^\bullet$HO radicals from hydrogen peroxide in 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 the European environmental regulations (EEC 76/4647, 1982) are the major drawbacks of this technology. In order to avoid the continuous loss of catalyst and the need of removing the iron after treatment, a growing research field focused on the immobilization of transition metals (especially iron species) over different supports is already undertaken by different research groups (Centi et al. 2000; Ovejero et al. 2001;

76 Guélou et al., 2003; Yuranova et al. 2004; Liou R.M. et al., 2005). In line with these works,

77 our research group has recently published a solid catalyst consisting of a crystalline

78 Fe_2O_3/SBA-15 nanocomposite which exhibits a high degradation rate for the mineralization

79 of phenolic aqueous solutions in a wide range of pH, using moderate amounts of oxidant and

80 with a remarkable stability of the iron oxides supported on the silica support (Melero et al.,

81 2007).

82

83   In addition to basic studies using target compounds as models, Fenton-like reactions

84 have been efficiently used as oxidation processes for the treatment of real industrial

85 wastewaters (Pérez et al., 2002-a and b; Ormad et al, 2006; Kurt et al., 2006; Bautista et al.,

86 2008), including pharmaceutical ones (Zgajnar and Zagorc-Konkan, 2005; Tekin et al., 2006)

87 resulting in a significant reduction of toxicity, improvement of biodegradability, and colour

88 and odour removal. Nevertheless, works described in literature have used homogeneous

89 Fenton reactions, maintaining the acidic medium and post-treatment steps to remove the iron

90 species.

91

92   A step forward is carried out in this work using a Fe_2O_3/SBA-15 material as Fenton-like

93 heterogeneous catalyst for the treatment of a pharmaceutical wastewater by catalytic wet

94 oxidation in presence of hydrogen peroxide (CWPO), in a continuous up-flow fixed bed

95 reactor (FBR). Continuous Fenton catalytic systems have been poorly dealt in literature in

96 comparison to, for instance, catalytic wet air oxidation processes using oxygen from air as

97 oxidant (Stüber et al., 2001; Álvarez et al., 2002-a, -b; Santos et al., 2005). Wastewater feed

98 flow rate, hydrogen peroxide concentration and initial pH of the inlet stream effect were

99 widely studied in order to determine the optimal reaction conditions that yielded to the highest

100 TOC degradation, as well as catalyst stability. To the best of our knowledge, the work

101 reported here is the first one dealing with the treatment of a real industrial wastewater by

102 CWPO process over a heterogeneous catalyst in a FBR.

103

104 **2. METHODS**

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106 *2.1. Pharmaceutical wastewater characterization*

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108   The wastewater has been obtained from a large scale drug and fine chemical

109 manufacturing industrial plant located in the south of Madrid, Spain. This industry is focused

110 on the synthesis of specific drugs for cardiovascular and venous diseases, as well as diabetes.

111 Table 1 shows the most relevant characteristics and composition of the pharmaceutical

112 wastewater. The wastewater presents a variable composition in time that makes hard to state

113 the organic compounds present in the stream. BOD_5/COD ratio reveals poor biodegradability

114 of the raw wastewater, whereas Average Oxidation State (AOS, Scott and Ollis, 1995;

115 Mantzavinos et al., 2000) indicates the presence of organic compounds with moderate

116 oxidation degree. At this point, it should be indicated that the wastewater selected for this

117 study is currently treated by a conventional homogeneous Fenton process with high excess of

118 oxidant and a considerable concentration of homogeneous iron and copper salts. This

119 homogeneous treatment exhibits a high organic degradation and comply the strict

120 environmental regulations but it has the above-mentioned drawbacks.

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126 **Table 1.** Main features of the 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
AOS (Average Oxidation Stage)	0.70

127

128 *2.2. Catalyst preparation and characterization*

129

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

139

140   For the preparation of the catalytic packed bed, Fe_2O_3/SBA-15 nanocomposite material

141   was extruded by blending the fresh powder catalyst (75 wt.%) with sodium bentonite (25

142   wt.%) and synthetic methylcellulose polymer which acts as binder in the extrusion process.

143   All the components were kneaded under high shear conditions until a homogeneous paste was

144   achieved adding controlled dosage of deionised water. Thereafter, the solid paste was placed

145   in a damp atmosphere, which provides the proper plasticity to be easily extrudable as well as

146   the needed cohesive properties (González-Velasco et al., 1999). Following, the paste was

147   passed through a 5 mm circular die using a ram extruder. The shaped-rod product was dried

148   for 3 days in a controlled temperature and humidity chamber with temperature and relative

149   humidity ranges of 20-40°C and 70-10%, respectively. After that, conformed catalyst was

150   calcined at 650°C in air for 2 hours, using a slow ramp of temperature to remove water

151   gradually, burning off the organic content and enhancing the mechanical strength of the

152   calcined extrudates by sintering of the inorganic binder (Martínez et al., 2007). The final

153   Fe_2O_3/SBA-15 pellets were obtained by crushing and sieving the extruded material to particle

154   sizes ranging from 1.0 to 1.6 mm. Table 2 summarizes the most relevant properties of the

155   extruded material, in comparison to the raw powder Fe_2O_3/SBA-15 sample.

156

157   **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

158   [a] Analyzed by laser scattering technique; [b] determined by N_2 adsorption isotherms at 77 K; [c] detected by ICP–AES; [d]
159   detected by X-ray diffraction; [e] sieving

160

161   According to previous works (Lázár et al., 2004; Martínez et al, 2005) the powder

162   catalyst can be described as a composite material that contains different iron oxides particles

163   (mainly crystalline hematite) embedded on a mesostructured SBA-15 matrix, and a little

164   amount of ionic Fe^{3+} species included in the framework by isomorphous substitution of Si

165   ions. Average particle diameter is 14.4 μm. The iron oxide particles are presented in a wide

166   distribution of sizes (30 − 3000 nm). The total iron content was around 19% wt., and the

167   support exhibits a BET surface area slightly lower than that usually found for pure SBA-15

168   (ca. 495 m^2/g and ca. 800 m^2/g, respectively) and a narrow pore diameter distribution centred

169   in 79 Å. On the other hand, extruded catalyst maintains the presence of crystalline hematite

170   entities as well as mesoscopic order and narrow pore diameter distribution typical of the SBA-

171   15 topology. Nevertheless, BET surface area decreases significantly in the extruded materials,

172   as **a** result of the presence of bentonite and sintering processes during the calcination step of

173   the extrusion process. Likewise, the existence of bentonite produces a slight solid dilution of

174   iron content in the extruded material.

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176   *2.3. Preliminary catalytic runs performed in a discontinuous stirred tank reactor (STR)*

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178   Preliminary catalytic wet peroxide oxidation experiments were performed in a 100 mL

179   glass autoclave reactor, with a total reaction volume of 75 mL, and mechanically stirred at

180   350 rpm. Appropriate amount of catalyst suspended in the wastewater (0.6 g/L) was placed

181   into the glass reactor. Then, the system was pressurised up to 7 bar with air and heated to the

182   selected reaction temperature. When the required temperature is achieved, the corresponding

183   amount of hydrogen peroxide is added to the reactor, and the reaction starts. Total reaction

184   time was fixed at 4 hours. Samples were withdrawn every 30 minutes and filtered through a

185   0.22 μm nylon filter.

186 *2.4. Catalytic runs performed in a continuous up-flow fixed bed reactor (FBR)*

187

188   The continuous CWPO experiments were conducted in an up-flow FBR working under

189 atmospheric pressure. The FBR consists of a jacketed glassware tube of 1.2 cm of inner

190 diameter and 15 cm of length. A catalyst mass (w_{cat}) of 2.9 g was placed in the catalytic

191 packed bed between two beds of spherical inert glass particles. An appropriate mixture of

192 wastewater and hydrogen peroxide was pumped to the packed bed reactor by means of a

193 Gilson 10SC HPLC pump operating at variable flow. The temperature of the system on the

194 upper part of the bed was controlled at 80ºC using an external recirculating heating bath with

195 a stream of silicon oil through the jacket of the glass reactor. Time zero is considered when

196 the feed flow reaches the top of the catalytic bed. The residence time for the liquid phase in

197 the packed bed reactor has been calculated following the procedure previously described in

198 literature taking into account the bed porosity (ε) and the liquid hold up (h_L) of the packed bed

199 (Martínez et al., 2007).

200

201 *2.5. Analytical techniques for water samples and reaction parameters*

202

203   Total organic carbon (TOC) content of the samples was analyzed using a

204 combustion/non dispersive infrared gas analyzer model TOC-V from Shimadzu. Residual

205 hydrogen peroxide in the samples was measured by iodometric titration. Finally, iron content

206 in the filtered solution after reaction was measured by ICP-AES analysis collected in a Varian

207 Vista AX spectrometer in order to determinate the leaching degree from the catalyst within

208 the effluent. Chemical Oxygen Demand (COD) was analyzed by a standard method using

209 potassium dichromate as oxidizing agent (APHA, 1998). Hydrogen peroxide interferes in

210 COD measurement overestimating the results obtained by the method. COD value eliminating

211 hydrogen peroxide interference can be obtained by the following equation (Kang et al., 1999):

212

213
$$COD = COD_m - 0.4706 \cdot [H_2O_2] \qquad (1)$$

214

215 where COD_m is the value obtained with standard method and $[H_2O_2]$ is the hydrogen peroxide

216 concentration detected in the measured sample by iodometric titration, all of them expressed

217 in mg/L. Finally, Biochemical Oxygen Demand (BOD) was defined as the amount of oxygen

218 consumed by the sample over 5 days at 20ºC, according to the appropriate standard method

219 (APHA, 1998), in mg of O_2/L. The performance of the reaction was studied following the

220 parameters described by equations 2 to 6.

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

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

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

221
$$\text{Biodegradability} = \frac{BOD_5}{COD} \qquad (5)$$

$$\text{Average Oxidation Stage (AOS)} = 4 - 1.5 \cdot \frac{COD}{TOC} \qquad (6)$$

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3. RESULTS AND DISSCUSION

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 out 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:

$$C + 2H_2O_2 \rightarrow CO_2 + 2H_2O \qquad (7)$$
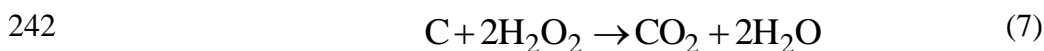
A molar ratio H_2O_2/C of 2, equivalent to a 5.6 mass ratio, is that necessary for the complete carbon depletion following the stoichiometry of the reaction. Taking into account the TOC content in the pharmaceutical wastewater (860 mg/L), the stoichiometric hydrogen peroxide concentration for its theoretical complete oxidation is ca. 4820 mg/L. Since wastewater might include other compounds susceptible to be oxidized by hydrogen peroxide, the stoichiometric H_2O_2/C mass ratio has been slightly increased up to 7. Reactions tests at two different initial hydrogen peroxide concentrations (5400 mg/L and 10800 mg/L, with H_2O_2/C mass ratio of 7 and 14, respectively) were performed obtaining TOC conversion

252 profiles depicted in Figure 1.a. TOC conversions are very close in both cases during the first

253 120 minutes of reaction. After this time, the benefits of an excess of oxidant are clearly

254 relevant, achieving ca. 55% of TOC degradation, in comparison to that obtained of ca. 40%

255 using 5400 mg/L, which is related with a complete conversion of the hydrogen peroxide for

256 the latter. Negligible TOC conversion was achieved in absence of oxidant.

257

258   On the other hand, the pH of the reaction medium has also a critical influence in Fenton-

259 like reactions (Melero et al., 2007). A pH between 3 and 4 is optimum for these types of

260 advanced oxidation processes. In order to evaluate the influence of the initial pH of the

261 aqueous solution in the STR, additional experiments were performed with acidified

262 pharmaceutical wastewater up to pH values of ca. 3, adding the appropriate amount of a

263 sulphuric acid solution (0.1 N). Figure 1.b shows TOC conversion profiles for reaction tests

264 carried out with an initial hydrogen peroxide concentration of 10800 mg/L and initial pH of 3

265 and 5.6, the later corresponds to the natural pH of the wastewater. The results reveal a slight

266 increase in the degradation rate with the decrease of the initial pH of the solution which is

267 more accentuated in the initial stages of the reaction. Note that a gradual decrease of the

268 aqueous solution pH up to ca. 2.6 is observed for both catalytic runs.

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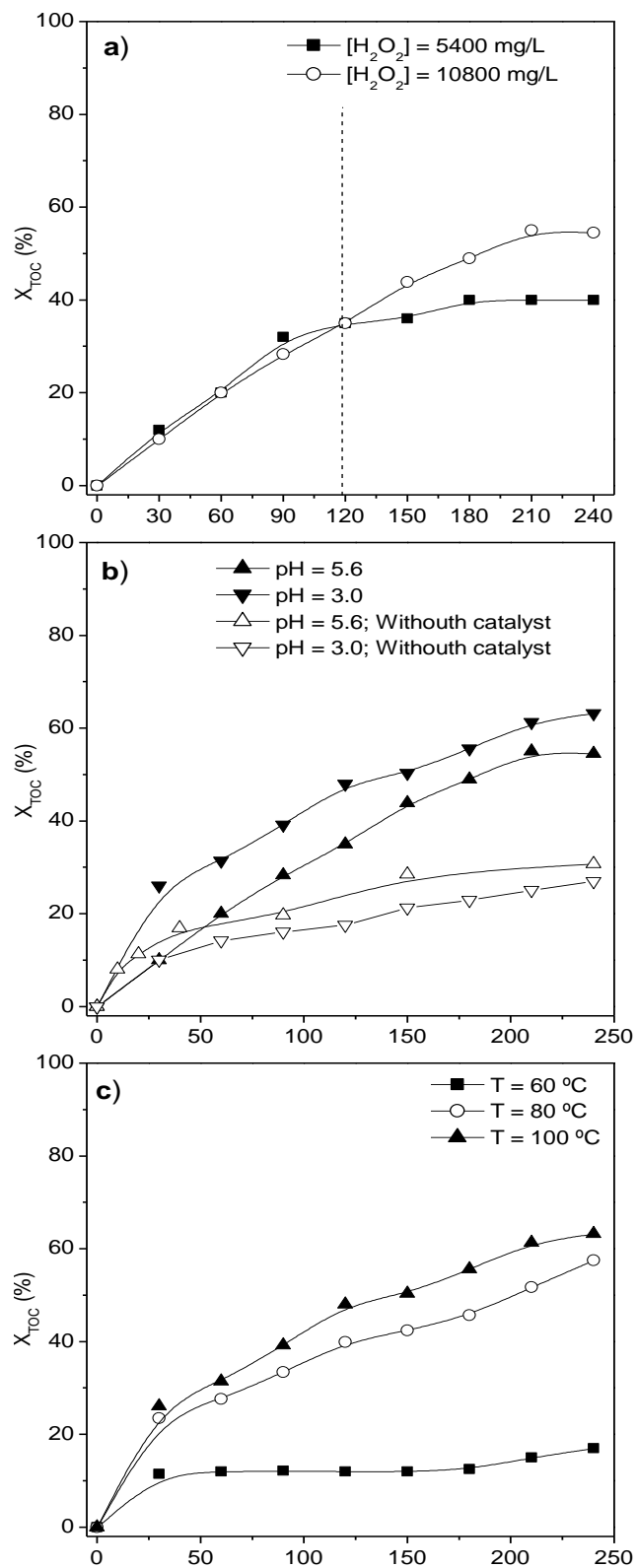
Fig. 1 – Catalytic runs in the STR(a) Influence of hydrogen peroxide concentration. T = 100
°C; pH_0 = 5.6; [catalyst] = 0.6 g/L.(b)Influence of initial pH. T = 100 °C; $[H_2O_2]_0$ = 10,800
mg/L; [catalyst] = 0.6 g/L (c) Influence of reaction temperature. pH_0 = 3; $[H_2O_2]_0$ = 10,800
mg/L; [catalyst] = 0.6 g/L.

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276   The effect of the reaction temperature in the activity of the heterogeneous catalytic

277   system was also studied. Figure 1.c shows TOC conversion profiles of reactions performed at

278   60, 80 and 100ºC, using 10800 mg/L of hydrogen peroxide and an initial pH of ca. 3. Results

279   reveal that a temperature of 80ºC is necessary to obtain an appreciable TOC degradation

280   along the process. An increase of temperature from 80 to 100ºC produces only a slight

281   increase in TOC conversion, especially at final reaction time (ca. 8%).

282

283   It is remarkable that in the reactions tests performed in this first part of the study, the

284   iron detected within the reaction medium after 240 minutes of reaction hardly reaches 6 mg/L,

285   which corresponds to the loss of ca. 6% of iron initially contained by the solid catalyst.

286   Particularly, the catalytic run carried out at 80ºC, initial pH of 3 and initial hydrogen peroxide

287   concentration of 10800 mg/L allows a TOC conversion of ca. 58% after 240 minutes,

288   accompanied with an iron leaching degree of 4.8%, which corresponds to a concentration of

289   iron in the reaction medium of ca. 4.8 mg/L.

290

291   Finally two blank reactions were performed in the absence of catalyst and two different

292   pH values (Figure 1.b). In both cases, the benefits of the catalyst are clearly evidenced,

293   showing a significant enhancement of the TOC degradation rate.

294

295   *3.2. Oxidation reactions of the real wastewater in a continuous fixed bed reactor*

296

297   Some of the reaction conditions fixed in this part of the work were selected according to

298   the results previously obtained in the STR, as well as the optimized conditions in the same

299   FBR system using phenol as model compound (Martínez et al., 2007). Thus, all the catalytic

300   runs were conducted in the FBR (L=15 cm and d_i = 1.2 cm) at 80ºC, under atmospheric

301 pressure, and using 2.9 g of catalyst mass. Likewise, an aqueous solution of the wastewater

302 (860 mg/L of TOC content) and hydrogen peroxide (10800 mg/L, equivalent to twice the

303 stoichiometric amount for the theoretical complete mineralization of the TOC content)

304 acidified up to pH 3 has been used as inlet stream. Following, the influence of other operation

305 variables will be discussed.

306

307 3.2.1. Influence of the feed flow rate

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309   In order to evaluate the influence of the residence time on the organic degradation, three

310 experiments were performed using feed flow rates of 0.25, 0.50 and 1.00 mL/min. These

311 flows provide residence times for the liquid phase of 3.79, 1.90 and 0.95 minutes, respectively

312 (Martínez et al., 2007). TOC and hydrogen peroxide conversion profiles along the time on

313 stream are depicted in Figure 2.a and 2.b.

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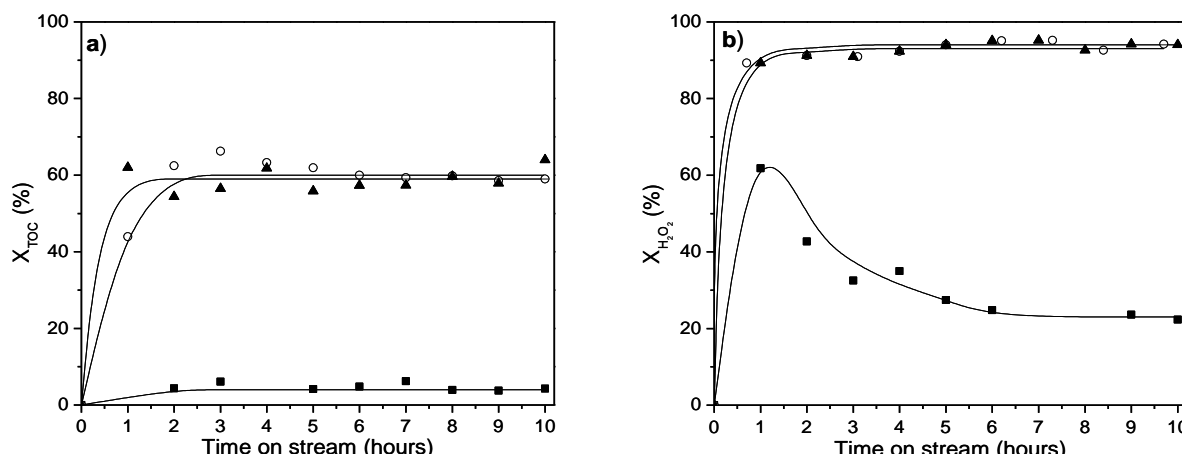
315
316 **Fig. 2** – Catalytic runs in the FBR. Influence of the residence time/feed flow rate on the TOC
317 (a) and hydrogen peroxide (b) conversions with time on stream. Reaction conditions: feed
318 flow rate (Q_{FEED}) ■ 1 mL/min; ○ 0.5 mL/min; : ▲ 0.25 mL/min; T = 80 ºC; w_{CAT} = 2.9 g;
319 $[H_2O_2]_{inlet}$ = 10,800 mg/L; pH_0 = 3.
320

321   An important effect can be seen when the feed flow rate is increased from 0.5 to 1

322 mL/min, (changing the liquid phase residence time from 1.90 to 0.95 minutes). A drastic

323 decrease in the TOC removal, almost inhibiting the oxidation process, is achieved with a feed

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324   flow rate of 1 mL/min. On the other hand, Figure 2.b reveals that an increase in the residence

325   time not only produces an enhancement of the TOC conversion, but also an important

326   increase in the hydrogen peroxide conversion, up to 90%. Likewise, comparison between

327   oxidant efficiencies reveals very low value ($\eta = 0.08$) for the higher feed flow rate, as

328   compared to that obtained when a feed flow of 0.5 mL/min is employed ($\eta = 0.25$).

329   Summarizing, a feed flow of 1 mL/min provides a low residence time which is not able to

330   promote an efficient organic degradation and as result the oxidant disappearance is mainly

331   related with a thermal decomposition. In contrast, the oxidant efficiency increases up to 0.25

332   when the feed flow rate is decreased until 0.5 mL/min, indicating that the oxidant is used

333   efficiently for the generation of hydroxyl radicals, enhancing the activity of the heterogeneous

334   catalytic system. Lowering the feed flow rate to 0.25 mL/min does not promote any

335   improvement on the catalyst performance, obtaining similar catalytic results in terms of

336   organic depletion (TOC conversion ca. 60 %) and oxidant efficiency (ca. 0.25). It seems that

337   there is a maximum TOC conversion (ca. 60 %) and higher residence times are not enough to

338   degrade refractory by-products formed during the organic depletion.

339

340   3.2.2. Influence of the hydrogen peroxide concentration in the inlet stream

341

342   In the preliminary experiments carried out in the STR, the initial hydrogen peroxide

343   concentration exhibited a high influence on the TOC degradation obtained after 240 minutes

344   of reaction time. As the reaction mechanism could be different in batch and fixed bed

345   reactors, due to the different catalyst-liquid ratio and contact (Bergault et al., 1997), the study

346   of the effect of the initial hydrogen peroxide concentration in the inlet stream has been also

347   considered for the FBR. Figure 4 shows the catalytic results in terms of TOC and hydrogen

348 peroxide conversions using oxidant concentrations in the inlet stream of 5400, 10800 and

349 16200 mg/L, corresponding to the stoichiometric loading, twice and three times, respectively.

350

351   A stoichiometric amount of oxidant yields a TOC degradation, around 40%, under

352 steady-state conditions. A hydrogen peroxide concentration twice the stoichiometric amount

353 (10800 mg/L) promotes an enhancement of the catalytic activity, allowing a steady TOC

354 degradation value of ca. 60%. A further increase in the oxidant loading does not enhance the

355 TOC degradation.

356
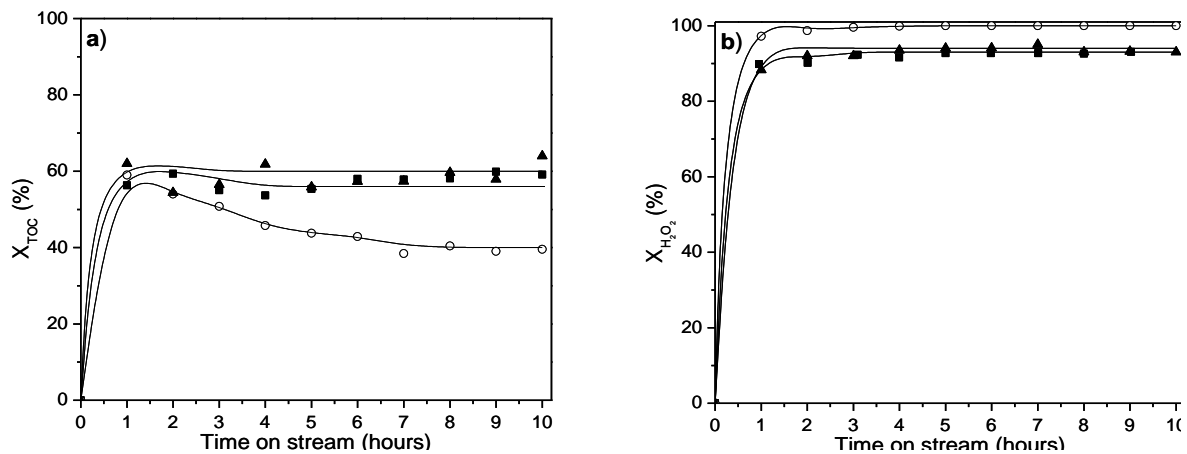
357

358 **Fig. 3** – Catalytic runs in the FBR: influence of hydrogen peroxide concentration in the inlet
359 effluent. TOC (a) and hydrogen peroxide (b) conversions with time on stream. Reaction
360 conditions: $[H_2O_2]_{inlet}$ -■- 16200 mg/L; -▲- 10800 mg/L; -○- 5400 mg/L; T = 80°C; Q_{FEED} =
361 0.25 mL/min; w_{CAT} = 2.9 g; pH_0 = 3.

362
363

364   As it has been mentioned previously, an important point in CWPO processes is the

365 efficiency in the use of the oxidant. The oxidant efficiency parameter (η) decreases gradually

366 with the increasing in the hydrogen peroxide loading in the feed (Table 3). But, whereas this

367 value hardly varies when the initial oxidant concentration is changed from 5400 mg/L to

368 10800 mg/L (0.33 and 0.26, respectively), there is an outstanding decrease when the hydrogen

369 peroxide loading is up to 16400 mg/L (η = 0.18). These catalytic results indicate that the use

370   of an initial oxidant concentration twice the stoichiometric amount allow obtaining a high

371   organic degradation with a reasonable use of the hydrogen peroxide. Upper oxidant loadings

372   in the feed stream do not improve the TOC degradation, yielding a worse use of the hydrogen

373   peroxide. Nevertheless, in all cases, the efficiency is far from the unit value (that means the

374   maximum efficiency in the use of the oxidant) which indicates that not all the oxidant is

375   efficiently used for the TOC mineralization due to the formation of intermediate compounds

376   more refractory to be oxidized or even scavenging reactions of the hydroxyl radicals.

377

378   Summarizing, Table 3 shows TOC and hydrogen peroxide conversions as well as

379   oxidant efficiency and iron concentration in the outlet effluent under steady state conditions

380   for the different feed flow rates and oxidant loadings studied. As discussed earlier, a feed flow

381   rate up to 0.5 mL/min and an oxidant loading twice the stoichiometric amount for a complete

382   carbon depletion enhance the TOC conversion and the efficient use of the oxidant. Likewise,

383   the iron species concentration in the outlet aqueous solution has been in all the cases below

384   the detection limit of the ICP-AES (0.05 mg/L). This data indicates a high stability of the iron

385   species supported over mesostructured material under the described reaction conditions.

386   Another important point is the hydrogen peroxide conversion, which is a crucial parameter for

387   a possible application in coupling oxidation-biological treatments. Under the optimized

388   conditions of this work, oxidant conversions close to 100% in the outlet stream are achieved,

389   making possible the integration with a biological system.

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395 **Table 3.** Influence of different operation variables for the treatment of a pharmaceutical
396 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		4	22	< 0.05	0.08
0.5	10800	58	94	< 0.05	0.25
0.25		60	94	< 0.05	0.26
	16200	61	94	< 0.05	0.18
0.25	10800	60	94	< 0.05	0.26
	5400	40	100	< 0.05	0.33

397

398 3.2.3. <u>Long-term reaction</u>

399

400   For an industrial application of this oxidation system is crucial that the catalyst keeps its

401 activity for long-term reactions. Fe_2O_3/SBA-15 extruded catalyst has shown high activity and

402 extreme stability of the supported iron species in all the above-discussed catalytic runs.

403 However, all the reactions were finished after 10 hours of time on stream. In order to

404 determine the feasibility of the catalyst for long-term continuous treatments, an additional

405 experiment was performed under the best reaction conditions (w_{CAT} = 2.9 g; T = 80ºC, Q_{FEED}

406 = 0.25 mL/min; $[H_2O_2]_{inlet}$ = 10800 mg/L, pH_{inlet} = 3), enlarging the time on stream up to 55

407 hours, being the catalytic results shown in Figure 4.

408

409   A slight decrease in the TOC conversion is observed after 20 hours of time on stream,

410 which is accompanied with a parallel decrease in the hydrogen peroxide consumption.

411 According to previous results published with this catalyst in the degradation of phenolic

412 aqueous solutions, the nature and environment of the iron active species might be modified

413 during the treatment (Martínez al., 2007). However, the loss of activity observed with this

414 industrial wastewater is less stressed than that previously observed with the same catalyst for

415 the degradation of phenolic aqueous solutions. Hence, although the deactivation of

19

416   Fe$_2$O$_3$/SBA-15 catalyst could be due to changes in the iron species toward less active ones

417   (Kong et al., 1998; Martínez et al., 2007), these iron environment changes seem to be

418   dramatically influenced by the features of inlet effluent. Nevertheless, it can be considered

419   that the catalyst keeps an almost constant activity after 55 hours on stream in the range of 50-

420   60 % TOC conversion, showing a high stability of iron species, and being the iron

421   concentration in the outlet effluent almost negligible. Likewise, the catalyst particles did not

422   grind during the process.

423
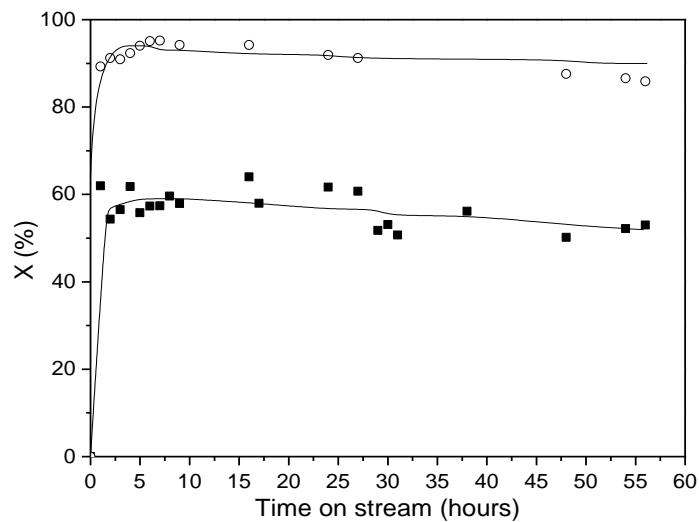
424
425   **Fig. 4 –** Catalytic runs in the FBR: long-term reaction. TOC (■) and hydrogen peroxide (○)
426   conversion with time on stream under selected conditions: T = 80ºC; w$_{CAT}$ = 2.9 g; [H$_2$O$_2$]$_{inlet}$
427   = 10800 mg/L; pH$_0$ = 3; Q$_{FEED}$ = 0.25 mL/min.
428
429   3.2.4. Characterization of the outlet effluent
430

431   In the final stage of the work, the exhaustive characterization of the outlet stream has

432   been carried out, being the results shown in Table 4. As result of the oxidation process, a

433   reduction in the amount of organic matter can be clearly observed. COD removal attained in

434   the system is about 81%. Interestingly, it can be seen that the chloride amount increases after

435   the treatment. The pharmaceutical wastewater could content chlorinated organic compounds

436   that can be degraded during the Fenton-like oxidation, releasing chloride ions into the reaction

437 medium (Gimeno et al., 2005). An outstanding increase in the biodegradability (in terms of

438 BOD_5/COD ratio) is also obtained after the treatment. This fact, as well as the increase in the

439 AOS parameter, indicates that some of the wastewater components have been transformed

440 into partially oxidized compounds, generally more biodegradable (Contreras et al., 2003).

441 Summarizing, the treatment of the pharmaceutical wastewater over Fe_2O_3/SBA-15

442 heterogeneous catalyst in a continuous up-flow fixed bed reactor results in a significant

443 reduction of organic matter, accompanied with an interesting enhancement of its

444 biodegradability. It should be pointed out that these results have been obtained using a

445 moderate loading of hydrogen peroxide and with a high stability of iron species.

446
447 **Table 4.** Pharmaceutical wastewater characterization after CWPO treatment.

Parameter	Inlet stream	Outlet stream
pH	5.6	3.6
COD (mgO_2/L)	1901	360
TOC (mg/L)	860	354
BOD_5 (mgO_2/L)	381	109
[Cl^-] (mg/L)	3380	7050
BOD_5/COD	0.20	0.30
AOS	0.70	2.35

448

449 Finally, the results obtained with the FBR reactor under steady-state conditions are

450 comparable with those achieved with a conventional treatment of the wastewater in the

451 pharmaceutical plant. In that case, a homogeneous and continuous Fenton-like system is

452 employed, with temperatures ranging from 70 to 80ºC, hydrogen peroxide concentrations

453 between 7000 and 12000 mgL^{-1}, initial pH of ca. 3 and a homogeneous catalyst consisting of

454 a mixture of Fe, Cu and Mn salts in concentration of 100-110 mgL^{-1}. Average TOC, COD and

455 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 are 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 with a remarkable stability of the supported iron species. The catalytic assay up to 55 hours on stream in a 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 has been achieved. BOD_5/COD ratio has increased from 0.20 up to 0.30, whereas the AOS has risen from 0.70 to 2.35. The enhancement of both parameters makes the wastewater more biodegradable and suitable of being treated by a conventional biological depuration system.

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