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# Azo-dye Orange II degradation by heterogeneous Fenton-like reaction using carbon-Fe catalysts

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## Abstract

In this work, the degradation and mineralization of the non-biodegradable azo dye Orange II (OII) was studied, making use of a heterogeneous Fenton-like oxidation process. For that, hydrogen peroxide activation was achieved by means of two different carbon-based catalysts, which have been impregnated with 7 wt% of iron. The carbon supports employed are quite different, one of them being an activated carbon prepared from agricultural by-products (olive stone), while the other one is a carbon aerogel, prepared by carbonization of an organic resorcinol–formaldehyde polymer. The solids have been characterized using several techniques, namely N<sub>2</sub> and CO<sub>2</sub> adsorption at -196 and 0 °C, respectively, mercury porosimetry, scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS). Then, the catalyst's performance in the Fenton-like oxidation of OII was compared, and the effects of the most relevant operating conditions (pH, catalyst concentration, H<sub>2</sub>O<sub>2</sub> concentration and temperature) analyzed for the most promising one (the carbon aerogel based catalyst). In this catalyst, characterization data point for a very good iron dispersion on the carbon surface. This sample showed very good catalytic performances, with mineralization degrees as high as 90%. However, iron leaching from the support is also considerable leading to a progressive deactivation in consecutive reaction cycles.

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# 1. Introduction

Pollution of water by dyes is a serious problem in the developed countries. Actually, the removal of dyes from wastewater is a challenge to the related industries, because the synthetic dyes used are stable compounds, difficult to destroy by common treatments. Physical, chemical, and biological methods are presently available for treatment of wastewater discharged from various industries. However, physical methods such as liquid–liquid extraction, ion-exchange, adsorption, air or steam stripping, etc., are ineffective on pollutants which are not readily adsorbable or volatile, and have further disadvantages because they simply transfer the pollutants to another phase rather than destroying them [1]. Activated carbon

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adsorption process for the removal of dyes is an accepted practice, but the cost of treatment might be high [2]. Ozone and hypochlorite oxidations as well as UV radiation/hydrogen peroxide processes are efficient decolourisation methods, but they are not desirable because of the high cost of equipment, operating costs and the secondary pollution arising from the residual chlorine [3]. In contrast, other advanced chemical oxidation methods can result in almost complete mineralization of organic pollutants and are effective for a wider range of organics. In particular, oxidation with Fenton's reagent which is based on ferrous ion and hydrogen peroxide — is a proven and effective technology for destruction of a large number of hazardous and organic pollutants [4]. Advantages of Fenton's reagent over other oxidizing treatment methods are numerous, including high efficiency, simplicity in destroying the contaminants (eventually leaving no residues), stability to treat a wide range of substances, non-necessity of special equipment, etc. [5]. Besides, operating conditions are usually

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mild (atmospheric pressure and around room temperature), and hydrogen peroxide is easy to handle and the excess decomposes to environmentally safe products [6].

The Fenton system uses ferrous ions as catalysts that react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing abilities [7,8]:

$$\mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{F}\mathrm{e}^{2+} \to \mathrm{H}\mathrm{O}^{\bullet} + \mathrm{O}\mathrm{H}^{-} + \mathrm{F}\mathrm{e}^{3+} \tag{1}$$

Generated hydroxyl radicals may then react with ferrous ions, for instance, to form ferric ions, or with the organics [9]:

$$Fe^{2+} + HO^{\bullet} \rightarrow OH^{-} + Fe^{3+}$$
<sup>(2)</sup>

$$HO^{\bullet} + Organics \rightarrow Products$$
 (3)

The oxidation products are usually low molecular weight compounds that are often more easily biodegradable or, in some instances, the organic compounds reduced to carbon dioxide and water, among other inorganics. However, it should be pointed out that the homogeneous Fenton process has a significant disadvantage: homogeneously catalyzed reactions need up to 50–80 ppm of Fe ions in solution, which is well above the European Union directives that allow only 2 ppm of Fe ions in treated water to be dumped directly into the environment [9]. In addition, the removal/treatment of the sludge-containing Fe ions at the end of the wastewater treatment is expensive and needs large amount of chemicals and manpower.

To overcome the disadvantages of the homogeneous Fenton or Fenton-like processes (the later one referring to the use of ferric rather than ferrous ions), the immobilization of the catalyst on inert support surfaces has been tried in order to avoid the catalyst-recovering step. Indeed, some attempts have been made to develop heterogeneous catalysts, prepared by incorporating Fe ions or Fe oxides into porous supports, subsequently used in a wide range of applications. Among others, it is worth mentioning the use of clays as supports for dyes degradation [10,11], of activated carbons for phenol [6], textile wastewaters [12] or 4-chlorophenol [13] oxidation, or of zeolites for phenol [14] or ethanol [15] oxidation.

This study concerns the degradation of the non-biodegradable azo dye Orange II by heterogeneous Fenton's reagent (a catalytic wet peroxide oxidation - CWPO - process) using carbon based-catalysts. Two different types of carbon materials were used as Fe supports: (i) an activated carbon (herein denoted as carbon H) prepared from agricultural by-products (olive stone) and (ii) a carbon aerogel (sample M) prepared by sol-gel technology. Both types of materials can be considered as examples of the classical and new carbon materials form. Both of them present different characteristics that could determine their applications: classical activated carbon are cheap materials prepared from very different raw precursors, but are heterogeneous materials with variable composition depending on the raw material used. On the contrary, carbon aerogels offer purity, homogeneity and controlled porosity, but are however more expensive because the synthesis method needs very specific equipment such as the supercritical drying. The performance of both materials was compared and the effect of the most relevant operating conditions in Fenton's oxidation evaluated. Orange II was selected as the test chemical to represent the concerned dye group because it is inexpensive and very much used in the textile, pulp and paper industries.

## 2. Material and methods

## 2.1. Preparation of the catalysts

Two different carbon materials were used as Fe-supports: an activated carbon and a carbon aerogel. The activated carbon was prepared from olive stones by carbonization of the raw material at 1123 K for 15 min in N<sub>2</sub> flow (300 cm<sup>3</sup>/min), and activation at 1123 K in CO<sub>2</sub> flow (300 cm<sup>3</sup>/min) to 22% of burn-off. The synthesis of the carbon aerogel involves the synthesis and carbonization of an organic aerogel prepared from resorcinol (R)-formaldehvde (F) polymerization in aqueous solution [16]. The polymerization and, therefore, the textural characteristics of the final aerogel strongly depend on the synthesis conditions [17]. In this case, the molar ratios employed for water (W), R, F and Na<sub>2</sub>CO<sub>3</sub> used as polymerization catalyst (C) were as follows: R/ F = 0.5, R/W = 0.07 and R/C = 300. The obtained pH was 6.5. Polymerization was allowed to proceed during seven days, controlling the temperature (25 °C in the first day, 50 °C in the second one, and 80 °C afterwards). After this period, the polymer was removed from the moulds and introduced in acetone for two days before the supercritical drying in CO<sub>2</sub>. The obtained aerogel was carbonized in N<sub>2</sub> atmosphere (100 cm<sup>3</sup>/min) at 500 °C for 5 h, increasing the temperature at a rate of 1.5  $^\circ$ C/min. Then, the oven was turned-off and the sample allowed to cool down in the same N<sub>2</sub> stream.

Finally, both supports were milled and screened and the fraction with a particle size smaller than 200  $\mu$ m impregnated by means of the classical impregnation method with aqueous solution, using ferrous acetate (FeAc<sub>2</sub>) as precursor. Thus, the amount of FeAc<sub>2</sub> needed for obtaining 7 wt% of iron in the final catalyst was dissolved in the minimum amount of water and added drop by drop on the corresponding carbon support. After impregnation, the samples were dried overnight at 100 °C and finally treated in N<sub>2</sub> flow at 200 °C for 2 h. TG and FTIR analyses showed that this thermal treatment is enough for the acetate decomposition.

# 2.2. Catalysts characterization

Textural characterization was carried out by N<sub>2</sub> and CO<sub>2</sub> adsorption at -196 and 0 °C, respectively, and mercury porosimetry. The BET surface areas ( $S_{\text{BET}}$ ) were calculated from the corresponding nitrogen adsorption isotherms. The micropore volume ( $W_0$ ) and mean micropore width ( $L_0$ ) were calculated by the application of the Dubinin–Raduskevich equation to CO<sub>2</sub> adsorption isotherms [18]. Mercury porosimetry was obtained up to a pressure of 4200 kg cm<sup>-2</sup> using a Quantachrome Autoscan 60 equipment. With this technique, the following parameters were obtained: pore size distribution of pores with a diameter greater than 3.7 nm; surface area of these pores, which will be referred to as external surface area,

 $S_{ext}$ ; pore volume corresponding to pores with a diameter between 3.7 and 50 nm,  $V_2$ , referred to as "mesopore" volume (one should note that the mesopore volume range is defined as 2–50 nm); pore volume of pores with a diameter greater than 50 nm, or macropore volume,  $V_3$ ; and particle density,  $\rho$ .

The morphology of the supports and catalysts was analyzed by scanning electron microscopy (SEM). Experiments were carried out with a ZEISS DSM 950 (30 kV) microscope. Metal dispersion and nature were followed by high-resolution transmission electron microscopy (HRTEM) using a Phillips CM-20 electron microscope and x-ray diffraction (XRD) using a Bruker D8 Advance diffractometer. Finally, x-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB 200A, VG Scientific (UK) system, with PISCES software for data acquisition and analysis. An achromatic Al (Ka) x-ray source operating at 15 kV (300 W) was used, and the spectrometer, calibrated with reference to Ag 3d5/2 (368.27 eV), was operated in CAE mode with 20 eV pass energy. Data acquisition was performed with a pressure lower then  $10^{-6}$  Pa. Spectra analysis was performed using peak fitting with Gaussian-Lorentzian peak shape and Shirley type background subtraction.

#### 2.3. Catalytic activity

Chemical oxidation of Orange II (Fluka p.a.) was carried out using 0.2 L of a 0.1 mM solution, in a jacketed glass batch reactor as described elsewhere [10,19]. Briefly, the reactor is provided with a magnetic stirrer and a thermostatic bath. After stabilization of temperature and pH, the powder catalyst was added followed by the H<sub>2</sub>O<sub>2</sub> solution (30% w/w, from Merck), this being considered the initial instant of reaction (t = 0). Absorbance, temperature and pH were then permanently measured. In particular, absorbance was monitored through a Philips PU8625 UV-vis spectrophotometer at 486 nm (characteristic wavelength of the Orange II molecule), which required the use of a flow-through cell and recirculation of the reaction mixture by a peristaltic pump. Along the reaction, the solution pH kept almost unchangeable ( $\pm$  0.1), which is certainly related to the low concentration of the Orange II solution used. Acquisition of data was carried out by means of a home-built interface using Labview 5.0 software, from National Instruments, with a frequency of 1/3 Hz (although in the OII concentration figures much less data are displayed, for a better visualization). Replicates of some of the experiments allowed to conclude that, for each run, experimental data do not differ, on average, more than 5% (maximum errors recorded in a single data were below 10%).

To evaluate the mineralization of the dye, total organic carbon (TOC) was measured using a Shimadzu 5000A spectrophotometer, model TOC-5000 CE, equipped with an automatic sample injector as described previously [10]. Reported TOC values represent the average of at least two measurements.

The total Fe in the solution was determined using a UNICAM 939/959 atomic absorption spectrophotometer.

## 3. Results and discussion

#### 3.1. Catalysts characterization

The morphology of the catalysts was analyzed by SEM. Their structures, which are defined by those of the corresponding supports, are shown in Fig. 1. The carbon aerogel structure (Fig. 1A) is composed by nearly spherical particles with smooth surfaces and nanometric size forming a network with "coral type" structure. According to its pore texture the microporosity is located into these primary particles, while the meso and macropore volume is determined by the inter-particle space, and therefore is related with the primary particle size, shape and overlapping degree [20]. The activated carbon morphology, shown in Fig. 1B, however presents a more heterogeneous appearance with large pores and large edges that come from the decomposition of the lignocellulosic materials. Both kinds of structures were previously observed in materials of similar origin [21,22].

Textural data of both supports are presented in Table 1. The BET surface areas of both supports obtained from the N<sub>2</sub> adsorption isotherms are similar. However, the CO<sub>2</sub> adsorption experiments, usually developed to study the narrowest microporosity [23], pointed out that support H has a more developed microporosity ( $W_0$ ,  $L_0$ ) favoured by the CO<sub>2</sub> activation process. On the contrary, the porosity range studied by mercury porosimetry is larger for support M. This support presents high values of meso ( $V_2$ ) and macropores ( $V_3$ ) volumes and a high external surface ( $S_{ext}$ ). Moreover, support H is



(A)

(B)

Fig. 1. SEM images of the carbon M-Fe (A) and H-Fe (B) catalysts.

Table 1 Textural data of the supports used

Sample	$V_2 ({\rm cm}^3/{\rm g})$	$V_3 ({\rm cm}^3/{\rm g})$	$W_0 ({\rm cm}^3/{\rm g})$	$L_0$ (nm)	$S_{\rm ext}  ({\rm m}^2/{\rm g})$	$S_{\rm BET}~({\rm m^2/g})$
Support M	1.02	0.99	0.19	0.61	337	641
Support H	0.12	0.41	0.29	1.10	55	691

mainly a macroporous material, and thus the external surface area is lower than for support M. The corresponding pore size distributions (PSD) are shown in Fig. 2. It is observed that support H presents a monomodal PSD centred in macropores with 150 nm of radius, while the typical porosity in carbon M are mesopores with 5 nm of radius.

The composition of both supports, determined by elemental analysis, is shown in Table 2. The main composition difference between both supports is due to the higher oxygen content of the carbon aerogel. It is well known that the chemical structure of R–F aerogels is defined by the formation of methyl and methyl–ether bridges between aromatic resorcinol structures, that also maintain unreacted –OH groups [20]. The low carbonization temperature of this carbon aerogels favour the high oxygen content observed which brings about a surface with a lower pHpzc than the activated carbon H.

The iron chemical state and dispersion were studied by XRD, XPS and HRTEM. When carbon H is used as support, the XRD pattern of the corresponding Fe-catalyst (Fig. 3) shows small and width diffraction peaks at  $2\theta = 35.48^{\circ}$ ,  $62.62^{\circ}$ ,  $30.12^{\circ}$ ,  $57.02^{\circ}$  and  $43.12^{\circ}$  that were assigned to  $(3\ 1\ 1)$ ,  $(4\ 4\ 0)$ ,  $(2\ 2\ 0)$ ,  $(5\ 1\ 1)$  and  $(4\ 0\ 0)$  planes of Fe<sub>3</sub>O<sub>4</sub> (JCPDS 88-0866), together with two broad bands, located at around 22 and  $42^{\circ}$ , associated to the 002 and 101 diffraction peaks of graphite, respectively. Obviously, only the latter can be found in the XRD analysis of the H support. When carbon M was used as iron



Fig. 2. Pore size distribution in the meso and macropore range of both carbon supports, obtained by mercury porosimetry.

Table 2 Elemental analysis of both supports (data given are in a weight percent basis)

Support	pHpzc	% C	% H	% N	% O	% Ash
Н	9.9	95.7	0.4	0.5	3.0	0.4
М	8.4	87.2	2.6	0.0	10.2	0.0

support, the XRD pattern do not present any diffraction peaks (Fig. 3). It is worth noting that the iron particles in this catalyst are difficult to detect even using HRTEM, as shown in Fig. 4. These results pointed out that in spite of the fact that Fe is well dispersed in both cases, dispersion is worse when support H is used, probably due to the smaller external surface area (cf. Table 1).

Looking at the information about the chemical state of iron on support M, the corresponding catalyst was analyzed by XPS. The surface metal content determined by this technique is 6.2 wt%, thus, taking into account that the total loading is 7.0%, it is also deduced that iron is uniformly distributed and highly dispersed. The XPS pattern of the Fe2p region is shown in Fig. 5. Two components are observed, located at 711.1 and 713.4 eV, respectively. These components are indicative of the presence of iron with different oxidation states and are consistent with the BE values previously published for magnetite (Fe<sub>3</sub>O<sub>4</sub>) [24] and ferric ions, either as hydrated (goethite, FeOOH) or anhydrous (Fe<sub>2</sub>O<sub>3</sub>) oxides [25,26], although in our case BE appear at around 0.5 eV higher. This



Fig. 3. XRD-patterns of the catalysts and of the H support.



Fig. 4. High-resolution transmission electron microscopy of the M-Fe catalyst.



Fig. 5. XPS patterns of the Fe2p region for catalyst M-Fe and deconvolution of the corresponding peaks (BE = 711 and 713 eV confirm the presence of Fe(II) and Fe(III)).

occurs because the neighbour atoms in a disperse system are fewer than in the bulk, and so the electrons are also fewer. The consequence is a less effective core-hole screening and the BE of the orbital shifts to higher energy [27].

## 3.2. Catalytic activity

#### 3.2.1. About the role of supports

Before comparing the behavior of both iron-containing catalysts, it is important to evaluate the OII elimination process, i.e., if OII removal occurs through adsorption, through a catalytic reaction or through both processes. For that reason, several runs were then performed.

The first one was a blank, carried out to evaluate the ability of  $H_2O_2$  to eliminate OII in aqueous solutions without the addition of any heterogeneous catalyst. Fig. 6 shows that OII degradation due to hydrogen peroxide is almost negligible (<1.0% after 4 h and 3.6% after 20 h), which might be attributed to its low oxidation potential as compared to hydroxyl or perhydroxyl radicals [28].



Fig. 6. Un-catalyzed orange II removal by hydrogen peroxide ( $C_{\rm H_2O_2} = 6 \text{ mM}$ ) and adsorption on supports H and M and iron catalysts, H-Fe and M-Fe ( $C_{\rm carbon} = 0.2 \text{ g/L}$ ,  $C_{\rm OII} = 0.1 \text{ mM}$ ,  $T = 30 \,^{\circ}\text{C}$ , pH 3.0).

To determine the influence of the adsorption processes experiments without  $H_2O_2$  were carried out. Fig. 6 shows that both carbon supports have a high adsorption capacity, being more important for carbon M (53.0 versus 34.5% after 20 h). The different adsorption capacities are related with the differences in the pore size distribution, thus the adsorption capacity is greater in support M in spite of the greater micropore volume of sample H, pointing out the importance of mesoporosity in the adsorption capacity of the catalysts is, in both cases, smaller than those of the corresponding support.

Whether this adsorption is an advantage or not, is not yet clear. While most authors consider that this preconcentration of the substrates to be oxidized in the vicinity of reactive centres is beneficial, Georgi and Kopinke [2] consider it to be a disadvantage because they claim that the predominant degradation pathway is the attack of  $HO^{\bullet}$  species on the organic contaminants fraction that is freely dissolved in the aqueous pore volume of the AC, whereas the adsorbed fraction is nearly unreactive.

Carbon materials are, moreover, good catalysts in different reactions [29,30]. For that reason, the catalytic behaviour of both supports was evaluated in the presence of  $H_2O_2$  (Fig. 7). The decolourization percentage increases regarding the adsorption conditions showing that both supports are catalytically active. The pollutant is however more deeply degraded in the presence of support H. Different aspects of the samples can contribute to this behaviour. First, the large microporosity of sample H, that is not accessible to the dye, can however favour the H<sub>2</sub>O<sub>2</sub> decomposition. On the other hand, it is well known that the interaction of carbon materials with pollutants in aqueous solution strongly depends on their surface chemistry [31]. In this sense, Khalil et al. [32], for instance, showed an inverse influence of surface area, pore volume and mean pore dimensions on the H<sub>2</sub>O<sub>2</sub> decomposition. Huang et al. [33] indicate that the H<sub>2</sub>O<sub>2</sub> decomposition was suppressed by decreasing the pHpzc of granular activated carbons, however, the degradation of 4-chorophenol by  $H_2O_2$  is enhanced by the



Fig. 7. Orange II removal through adsorption and through oxidation on both carbon supports and catalysts (T = 30 °C, pH 3.0,  $C_{\text{carbon}} = 0.2$  g/L,  $C_{\text{H}_2\text{O}_2} = 6$  mM).

same acid groups. Finally, Oliveira et al. [34] indicate that basic sites generated during  $H_2$  pretreatment at different temperatures enhanced the formation of HO<sup>•</sup> species from  $H_2O_2$ .

Our results are therefore in good agreement with these conclusions. The catalytic activity of the supports seems to be more directly related with their different surface chemistry. The greater activity of support H is favoured by its heterogeneous structure, and greater basic character pointed out by the values of pHpzc (Table 2).

# 3.2.2. Influence of the experimental conditions in the ironsupported catalysts performance

Although the results summarized in Fig. 7 puts into evidence the possibility of using directly carbon supports as catalysts, the catalytic role of iron is clearly evidenced in this section when one compares the performances shown by the supports with those exhibited by their corresponding Fe-catalysts. Actually, while with the best support (support H) one needs 15–20 h to reach high OII degradation levels (>95%), with the Fecatalysts this can be achieved in only ca. 1.5–3 h in the same experimental conditions. Thus, while the use of carbon materials as catalysts can present several advantages such as lower price or no leaching of metallic pollutants, the use of iron catalyst is necessary when operation time should be shortened. The parameters that control their catalytic performance will be studied below.

3.2.2.1. Influence of pH. The catalytic performances of Fecatalysts are obviously better than their corresponding support. It is well-known that this metal is able to transform  $H_2O_2$  into HO<sup>•</sup> species [7]. Fig. 8 shows a comparative performance of both catalysts at different pH values. It is noteworthy that the M-Fe catalyst is more active than the H-Fe one at any pH studied (between 2 and 4) in spite of the greater catalytic activity of support H. This fact should be related with the better dispersion of Fe into the large external surface provided by mesoporosity of sample M, although the hypothesis that the larger adsorption capacity of this sample can favour the degradation of pollutants in neighbour Fe particles cannot be ruled out. The importance of the iron dispersion in composite materials for Fenton oxidation was also pointed out by other authors [35].

With both catalysts used, the higher the pH (in the range 2– 4), the slower is the reaction rate (Fig. 8A). For catalyst M-Fe, dye degradation at pH 2 or 3 proceeds at almost the same rate, being practically complete after 2 h of reaction. This is an important advantage because it allows using less acid to acidify the medium. It must be stressed that another experiment, performed at pH 1 with the M-Fe catalyst, showed a marked decrease in the performance: 72.2% after 4 h.

In terms of TOC removal (Fig. 8B), conclusions are similar as for OII degradation: for both carbons, a better performance is reached when the pH is lower. In addition, catalyst M-Fe always shows better performances as compared to H-Fe, reaching mineralization degrees after 4 h above 80%. Thus, while almost total elimination of OII pollutant is achieved, its oxidation produces intermediate products of which mineralization is not



Fig. 8. pH effect on the degradation of OII solution (A), in TOC removal (B) and in iron leaching (C) using M-Fe and H-Fe catalysts (T = 30 °C,  $C_{cat.} = 0.2$  g/L,  $C_{H_2O_2} = 6$  mM).

complete at any pH. The worst performance of both samples at high pH values can be ascribed to the stability of  $H_2O_2$ , which starts to rapidly decompose into molecular oxygen without formation of appreciable amounts of hydroxyl radicals [36]. In the mild operating conditions used, it is expected that the formed  $O_2$  is not capable to efficiently oxidize the organics.

Another important parameter to quantify is the iron leaching, which should ideally be null to provide long-term stability. Fig. 8C shows that leaching increases when the medium is more acid. This result is in agreement with other authors [6,37]. Carbon M shows slightly higher iron lixiviation, especially at pH 2, what is probably related with the better dispersion and accessibility of Fe-particles. On the other hand, the activity of the leached iron could, in part, explain the better performance of this sample. However, not only the homogeneous but also the heterogeneous process is of importance. This can be concluded from the OII degradation and mineralization degrees at pH 2 or 3, which are similar (Fig. 8A and B), in spite of the higher Fe loss from the support for pH 2 versus pH 3 [6.9% versus 10.1% after 4 h for carbon M, where the values refer to the amount (wt%) of Fe lost as refereed to the total Fe initially present in the catalyst].

It can therefore be concluded that the better experimental conditions are reached using pH 3 with sample M, where the OII degradation is similar than at pH 2, but lower iron leaching is produced. The subsequent runs will consequently be carried out at pH 3 using the best sample: the Fe-M catalyst.

3.2.2.2. Effect of the catalyst concentration. As expected, when the amount of catalyst employed increases, OII and TOC elimination rates also increase (Fig. 9A and B), due to the increasing amount of active sites for  $H_2O_2$  decomposition and, less important but also of concern, for organic compounds adsorption. Nevertheless, the maximum mineralization reached is around 90% (only attained for a catalyst concentration of 0.30 g/L at t = 4 h), although decolourisation is almost complete for any catalyst concentration used. Moreover, while

differences in terms of dye removal for catalyst concentrations between 0.2 and 0.3 g/L are not too significant, TOC removal homogeneously increases with the catalyst concentration. It is also noteworthy that, as found by other authors [6], a high reduction of TOC is observed at the reaction beginning, but the rate of mineralization slows down possibly due to the lower oxidation rate of reaction products and the development of parallel reactions between excess ferrous iron and hydroxyl radicals (see Eq. (2)), or to the scavenging of those or other radicals by present iron species [7,38,39]:

$$FeOH^+ + HO^{\bullet} \rightarrow Fe^{3+} + 2OH^-$$
(4)

$$\mathrm{Fe}^{2+} + \mathrm{HO}_2^{\bullet} \to \mathrm{Fe}^{3+} + \mathrm{HO}_2^{-} \tag{5}$$

$$Fe^{3+} + HO_2^{\bullet} \to Fe^{2+} + O_2 + H^+$$
 (6)

These undesirable reactions may also account for the very similar OII history profiles in Fig. 9A when the catalyst concentration is 0.20 or 0.30 g/L. For this reason, subsequent runs will be performed using a catalyst concentration of 0.20 g/L.

Finally, iron concentration in solution increases with the amount of M-Fe catalyst used (Fig. 9C), reaching however values always below EU guidelines (<2 ppm), even when using a catalyst concentration of 0.3 g/L. In terms of percentage of iron lost from the solid, referred to the total Fe initially incorporated, Fig. 9D shows that differences are small, i.e., the



Fig. 9. Effect of catalyst concentration in the degradation of OII solution (A), in TOC removal (B), in iron concentration in solution (C) and in percentage of iron lost by the M-Fe catalysts (D) (T = 30 °C, pH 3.0,  $C_{H_{2}O_{7}} = 6$  mM).

percentage of iron that has been leached out does not depend on the catalyst concentration employed in the catalytic runs.

3.2.2.3. Effect of the hydrogen peroxide concentration. The effect of the hydrogen peroxide was analysed by varying its initial concentration between 3 and 48 mM. According to Feng et al. [37], 42 mol of  $H_2O_2$  are theoretically needed to completely degrade 1 mol of the dye  $(C_{16}H_{11}N_2NaO_4S + 42H_2O_2 \rightarrow 16CO_2 + 46H_2O + 2HNO_3 + NaHSO_4)$ . Based on this, the concentrations employed are between 0.71 and 11.4 (molar ratio) of the overall stoichiometry for the complete mineralization of OII.

Increasing H<sub>2</sub>O<sub>2</sub> load from 3 to 6 mM increases reaction performance (Fig. 10A and B) because more radicals are formed. However, a significant improvement is not seen for a higher concentration ( $C_{H_2O_2} = 24 \text{ mM}$ ). Moreover, performance either in terms of OII degradation or in terms of mineralization drops down for an excessive peroxide load ( $C_{H_2O_2} = 48 \text{ mM}$ ) due to the well-known hydroxyl radicals scavenging effect [7,38]:

$$\mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{HO}^{\bullet} \to \mathrm{H}_{2}\mathrm{O} + \mathrm{HO}_{2}^{\bullet} \tag{7}$$

Such reaction reduces the probability of attack of organic molecules by hydroxyl radicals, and causes the oxidation rate to drop. Although other radicals  $(HO_2^{\bullet})$  are produced, their oxidation potential is much smaller than that of the HO<sup>•</sup> species [28]. Therefore, in the subsequent runs,  $C_{H_2O_2} = 6$  mM will be used.

Fig. 10C evidences that H<sub>2</sub>O<sub>2</sub> concentration does not seem to affect iron leaching. This is in agreement with some works found in the literature either with Fe- [40] or Cu-based catalysts [41], showing however that the leaching experiments are nicely reproducible (lines for different runs practically overlap). It is however important to highlight that iron leaching increases from 3 to 4 h of reaction, a behaviour that can also be noticed in other figures, e.g., Fig. 9. In spite of the fact that the total amount of iron in the system is the same, a larger fraction is in solution, from which one could expect an increase in the mineralization degree. However, such trend is not accompanied by a significant change in TOC removal, which might indicate that the products formed are refractory, hard to further oxidise. Sotelo et al. [41] also pointed out the formation of refractory compounds in the second stage of the degradation kinetics, which showed a fast removal stage followed by a slower second step where TOC conversion is levelled off.

3.2.2.4. Effect of the reaction temperature. When the temperature of the reaction medium is increased, oxidation proceeds at a faster rate (Fig. 11A and B) due to the exponential dependence of the kinetic constants on it (Arrhenius law), as shown below. However, after ca. 1.5 h, dye degradation is similar for temperatures in the range 30–70 °C (Fig. 11A), with almost 100% decolorisation.

The mineralization degree increases with increasing temperature, although total mineralization is not attained even at 70 °C. The most significant difference is noted when reaction temperature increases from 10–30 °C (Fig. 11B). In this



Fig. 10. Hydrogen peroxide concentration effect on the degradation of OII solution (A), in TOC removal (B) and in iron leaching (C) using M-Fe catalysts (T = 30 °C, pH 3.0,  $C_{cat.} = 0.2$  g/L).

temperature range TOC removal increases from ca. 50 to almost 80%, however, each progressive 20 °C increase only produces around 3% of TOC increase. This is possibly due to the accelerated thermal decomposition of  $H_2O_2$  into oxygen and water [1,42,43]. For this reason, final experiments will be carried out at 30 °C. In addition, the higher the reaction



Fig. 11. Temperature effect on the degradation of OII solution (A), in TOC removal (B) and in iron leaching (C) using M-Fe catalysts ( $C_{H_2O_2} = 6 \text{ mM}$ , pH 3.0,  $C_{\text{cat.}} = 0.2 \text{ g/L}$ ). Plot (D) represents the temperature dependence of the apparent pseudo-first order kinetic constant.

temperature, the higher the iron lost from the catalysts (Fig. 11C), in agreement with other studies reported in the literature [6].

Assuming, as commonly found, a pseudo-first order for the dye degradation, the mass balance in the batch reactor yields:

$$V\frac{\mathrm{d}C_{\mathrm{OII}}}{\mathrm{d}t} = -(-r_{\mathrm{OII}})W = -k_{\mathrm{ap}}C_{\mathrm{OII}}W \tag{8}$$

where  $C_{\text{OII}}$  is the orange II concentration at instant *t*,  $k_{\text{ap}}$  is the apparent pseudo-first order kinetic constant, *W* is the mass of catalyst and *V* is the reaction volume. Integration of such equation provides the theoretical history profiles:

$$C_{\rm OII} = C_{\rm OII_0} \exp\left(-k_{\rm ap} \frac{W}{V}t\right) \tag{9}$$

to which the data shown in Fig. 11A were fitted. The fittings  $(R^2 > 0.99)$  at different temperatures were performed using

data up to 95% OII conversion, except for T = 10 °C, where all data have been used. The dependence of the kinetic constant on the reaction temperature shown in Fig. 11D evidences an Arrhenius behaviour, with an activation energy of 56.1 kJ/ mol. Others authors [44] have found the same dependence with the temperature in a photo-assisted process through a Fe/C structured catalyst for the degradation of orange II, and in this case the value of the activation energy for the dye discoloration was 47.4 kJ/mol (in a similar temperature range).

3.2.2.5. Stability and recycling of the Fe-M catalyst. In practice, to use a heterogeneous catalyst in Fenton-like oxidation, it is crucial to evaluate the stability of the solids. With that goal in mid, consecutive experiments were performed with the same sample, recovered by filtration after each cycle. Fig. 12 shows that after the first two experiments, reaction performance, particularly OII degradation rate, is significantly

Table 3

Comparison of reaction performance in terms of OII degradation, OII mineralization and iron leaching of the carbon catalysts with two clay-based samples [10]<sup>a</sup>

Sample	OII degradation, t = 2 h (%)	OII degradation, t = 4 h (%)	TOC removal, t = 4 h (%)	Iron leaching, $t = 4 \text{ h} (\text{mg/L})^{\text{b}}$
M-Fe	79.0	94.6	58.8	0.642 (10.0%)
H-Fe	26.2	55.0	23.0	0.498 (7.8%)
Clay oxalate	35.9	92.9	70.3	0.190 (2.6%)
Clay acetate	30.5	79.3	66.7	0.558 (7.5%)

<sup>a</sup> Reaction conditions: T = 30 °C, pH 3.0,  $C_{H_2O_2} = 6$  mM,  $C_{catalyst} = 91.5$  mg/L.

<sup>b</sup> Percentage values refer to the amount (wt%) of Fe lost into the solution after reaction, based on the total iron initially present in the samples.



Fig. 12. Effect of consecutive experiments with the M-Fe catalyst on the degradation of OII solution (A), in TOC removal (B) and in iron leaching (C) ( $C_{H_2O_2} = 6 \text{ mM}$ , pH 3.0,  $T = 30 \degree$ C,  $C_{cat.} = 0.2 \text{ g/L}$ ). Oxidation performance is also compared with homogeneous catalytic process, using iron(II) or iron(III) salts (1.5 mg/L).

affected. Mineralization is also affected, with values after 4 h of reaction decreasing in the three consecutive cycles from 76.5 to 71.4 and finally to 55.9%, respectively. This is in part a consequence of the iron lost from the support, which amounts to 24% of the initial iron after the three cycles (ca. 8% per cycle, cf. Fig. 12C).

The iron leaching is not the only reason for the observed activity decay. Actually, based on the effective amount of iron available at the beginning of each cycle, the initial reaction rates have been computed (using Eq. (8) for t = 0). The values obtained for the three consecutive cycles ( $5.5 \times 10^{-6}$ ,  $4.0 \times 10^{-6}$  and  $1.1 \times 10^{-6}$  mmol s<sup>-1</sup> mgFe<sup>-1</sup>, respectively) show that iron deactivation is also produced, although the reasons behind that are not yet clear and will be the aim of future work. Zazo et al. [6] attributed the Fe-active carbon catalyst deactivation observed to Fe complexation by oxalic acid (resulting from phenol oxidation) and/or to active sites blockage due to polymeric deposits, with partial reactivation being reached after washing with 1N NaOH solution.

Based on the amount of iron lost from the M-Fe catalyst after the first cycle, two experiments were performed in homogeneous phase using iron salts in similar concentration as that produced by leaching (1.5 mg/L). From Figs. 12A and B one can clearly seen that both OII degradation and particularly mineralization with the iron salts proceeds much slower than with the carbon-based catalyst, i.e., the iron (in the 2+ or 3+ oxidation state) present in solution is not capable to catalyze the process so efficiently. Therefore, the process studied in this work using the carbon-based catalysts is essentially heterogeneous, not homogeneous. Finally, the faster reaction rate with Fe(II) versus Fe(III) salts (Fig. 12A and B) is due to the faster reaction with hydrogen peroxide in Fenton (reaction with ferrous iron) compared to Fenton-like (reaction with ferric iron) processes [45–47].

Finally, due to reasonable performances reached by the carbon catalysts, we decided to compare them with catalysts based on pillared saponite impregnated with iron salts, reported in a previous work [10]. Then, the carbon-based catalysts were tested in identical conditions as clays, which contain the same iron content (ca. 7-8 wt%). Table 3 shows that in terms of OII degradation or TOC removal, the final performance (t = 4 h) of the M-Fe catalyst is similar to that found with the best of the clays, i.e., the one using the iron(II) oxalate salt as precursor. However, OII degradation proceeds at a much faster reaction rate with the aerogel catalyst (cf. values for t = 2 h). Once again, carbon H-Fe presents a worst performance. However, one important disadvantage of the carbon catalysts is the amount of iron lost from the support, which is much higher than that reached with the oxalate clay sample. Nevertheless, if one compares the iron leaching of the carbon catalysts with that of a clay sample in which the iron precursor was the same as in the carbons catalysts, i.e., acetate, it turns out that iron lixiviation data become similar, even though catalytic performance of this other clay is worst (Table 3). It seems therefore that the precursor used might have an important role in fixing the iron to the support. For that reason, future work will be focused towards the optimization of the iron precursors during preparation of Fenton-like catalysts in carbonaceous supports.

## 4. Conclusions

Two carbon samples have been employed as supports for iron particles with the aim of using them in the Fenton-like oxidation of Orange II, an azo dye. The carbon samples used are quite different, a classical activated carbon (sample H) and a carbon aerogel (sample M). They differ largely in the porosity: while carbon H is a macro and microporous material, carbon M has a large mesopore volume. Chemically, the carbon aerogel has a greater oxygen content, which brings about a lower pHpzc value. The adsorption capacity depends on the textural characteristics, while the catalytic activity in the Orange OII degradation is mostly related with the chemical ones.

The catalysts have been prepared through wet impregnation using ferrous acetate. The XPS and XRD experiments showed that Fe presents different oxidation states (Fe (II) and Fe (III)) that is more dispersed in the case of support M because of the large mesopore volume and external surface area of this sample.

The good iron dispersion in the carbon M sample may be one reason for the better catalytic behaviour of this sample in the Fenton-like process. Indeed, the Fe-doped aerogel showed better catalytic performances, mainly higher reaction rates, than those reached with the activated carbon catalyst.

With both activated carbon-based catalysts, OII elimination is due to two processes — adsorption and catalysis — the last being the most relevant one. Although a homogeneous catalytic contribution also exists, as a consequence of the iron leaching, the process is essentially heterogeneous. When choosing the reaction conditions, one has to find a compromise between high reaction performances, with low iron leaching. For that reason, it is advisable to operate at pH around 3.0, T = 30 °C, and a hydrogen peroxide concentration of 6 mM (for a dye concentration of 0.1 mM).

The catalysts studied have however an important limitation for their use in industrial practice — the high iron loss from the supports. To overcome this, it is advisable to use the preparation of carbon aerogels in which iron is within the aerogel structure. Nevertheless, even in the worst conditions tested the iron concentration in solution is always bellow the EU guidelines (<2 ppm) and the catalytic performances reached are quite good, with mineralization degrees as high as 90%, for catalysts concentration not higher than 0.20 to 0.30 g/L. Decolourisation might however be almost complete. This means that the dye is being transformed into intermediate products that evolve towards CO<sub>2</sub> and H<sub>2</sub>O as the reaction proceeds, remaining however some refractory compounds.

Finally, consecutive experiments performed with the M-Fe sample showed some activity decay, which is due to both iron leaching and catalyst deactivation.

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