Decolourisation of dye solutions by oxidation with H_2O_2 in the presence of modified activated carbons

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ABSTRACT

The decolourisation of dye solutions by oxidation with H_2O_2, using activated carbon as catalyst, is studied. For this purpose, three different samples, mainly differing in the respective surface chemistries, were prepared and characterized. Moreover, this work involved three pH levels, corresponding to acid, neutral and alkaline solutions, and six dyes belonging to several classes. The catalytic decolourisation tests were performed in a laboratorial batch reactor. Adsorption on activated carbon and non-catalytic peroxidation kinetic experiments were also carried out in the same reactor, in order to compare the efficiencies of the three processes. The non-catalytic reaction is usually inefficient and, typically, adsorption presents a low level of decolourisation. In these cases, the combination of activated carbon with hydrogen peroxide may significantly enhance the process, since the activated carbon catalyses the decomposition of H_2O_2 into hydroxyl radicals, which are very reactive. Based on the experiments with the different activated carbon samples, which have similar physical properties, it is proved that the surface chemistry of the catalyst plays a key role, being the basic sample the most active. This is discussed considering the involvement of the free electrons on the graphene basal planes of activated carbon as active centres for the catalytic reaction. Additionally, it is shown that the decolourisation is enhanced at high pH values, and a possible explanation for this observation, based on the proposed mechanism, is given.

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1. Introduction

One of the main problems found in the decontamination of textile effluents is the removal of colour. When introduced in water courses, the highly coloured components resulting from the incomplete fixation of dyestuffs on textile substrates may cause significant disturbance in the ecological systems, beyond the undesirable aspect of the receiving waters [1]. Furthermore, several studies have shown that some of those compounds are highly carcinogenic [2,3]. Hence, degradation of organic dyes is necessary from a point of view of public health and safety.

Due to the variability of the organic dyes used and the corresponding effluents, there is a wide range of treatment techniques for this type of wastewater. Most of them include an initial step of activated sludge treatment to partially remove the organic matter, followed by oxidation (usually with ozone [4], Fenton's reactant [5] or H_2O_2/UV [6]), or by membrane separation [7], or by adsorption on activated carbon [8,9]. Despite this variety, there is no single process capable of adequate treatment, due to the complex nature of these effluents [10]. Hence, the better solution for textile wastewater treatment is a combination of different techniques.
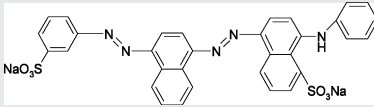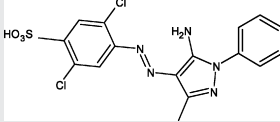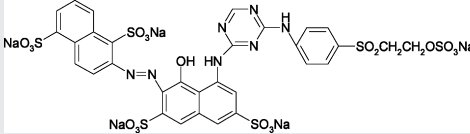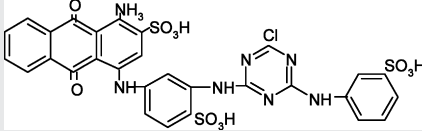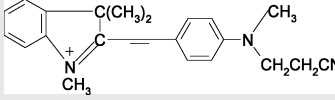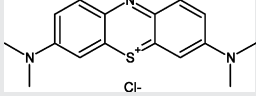
Environmentally, H_2O_2 is a friendly oxidant. Recent studies [11–13] indicate that the combination of H_2O_2 and activated carbon into a single process could offer an attractive alternative for coloured wastewater treatment. This type of procedure combines adsorption and catalysis in a single step, taking advantage of the performance of activated carbon as adsorbent and catalyst (mainly resulting from its large surface area and flexibility, i.e. the possibility of tailoring the porous structure and the surface chemical properties for a specific application). One disadvantage of the process is the risk of saturation and/or deactivation of the catalyst, which would require regeneration or complete replacement. The studies in this area proposed reaction mechanisms that involve the formation of $HO^\bullet$ radicals, justifying the inclusion of this type of treatment in the group of advanced oxidation processes.

In this work, the decolourisation kinetics of different dye solutions was studied in a laboratory scale batch reactor by three different processes: adsorption on activated carbon, non-catalytic oxidation with H_2O_2 and oxidation with H_2O_2 in the presence of activated carbon. The main goal of this study is to evaluate the synergic effect between H_2O_2 and activated carbon in the oxidation of

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Table 1
Main characteristics of the selected dyes

Class	Commercial and generic name	Molecular structure	Chemical class	λ_{max} (nm)
Acid	Erionyl Navy R, CI Acid Blue 113		Diazo	566
Acid	Telon Light Yellow FG, CI Acid Yellow 49		Monoazo	402
Reactive	Rifafix Red 3BN, CI Reactive Red 241		Monoazo	540
Reactive	Cibacron Blue BR, CI Reactive Blue 5		Anthraquinone	597
Basic	Astrazon Brilliant Red 4G, CI Basic Red 14		Cyanine	513
Basic	Methylene blue, CI Basic Blue 9		Thiazine	664

organic dyes, considering in the analysis both the initial solution pH and the surface chemistry of the carbon material.

2. Materials and methods

2.1. Preparation of modified activated carbons

The starting material used in this work is the activated carbon Norit GAC 1240 PLUS (granulates with diameters between 0.42 and 2.0 mm). This material was submitted to different modifications, using well-established procedures such as the oxidation with HNO_3 and the thermal treatment with H_2, in order to produce samples with different surface chemistries, while maintaining the original textural properties as far as possible. The samples are labelled as follows: ACo: activated carbon Norit GAC 1240 PLUS; ACa: sample ACo oxidized in the liquid phase with HNO_3 6 M at boiling temperature for 3 h, using a Soxhlet extraction apparatus; ACb: sample ACa thermally treated under H_2 flow at 700 °C for 3 h plus 1 h under dry air flow at room temperature. A detailed description of these treatments can be found in Pereira et al. [8].

2.2. Characterization of the activated carbon samples

The textural and surface chemical properties of the activated carbon samples were obtained by the following techniques, as described elsewhere [9]: N_2 adsorption at 77 K, determination of acidity, basicity and pH_{pzc}, and temperature programmed desorption (TPD). XPS analyses of sample ACo before and after reaction were also performed, in order to evaluate the possible effect of the prolonged contact with hydrogen peroxide during reaction on the surface chemistry of the catalyst.

2.3. Chemicals

The coloured effluents were simulated considering various dyes belonging to different classes: CI Acid Blue 113, CI Acid Yellow 49, CI Reactive Red 241, CI Reactive Blue 5, CI Basic Red 14 and methylene blue. Their main characteristics are shown in Table 1. The textile anionic dyes CI Acid Blue 113 and CI Reactive Red 241 were analysed with particular detail. The respective stock solutions were prepared by dissolving a selected amount of each dye in deionised water.

Hydrogen peroxide (30%, w/w) was obtained from Fluka. Other chemicals were of analytical reagent grade and were used without further purification.

2.4. Decolourisation experiments

All the experiments were carried out at room temperature in a laboratorial stirred reactor (800 mL). The influence of both the initial pH (3 and 7 for CI Acid Blue 113 and 3, 7 and 10 for CI Reactive Red 241) and the surface chemistry of activated carbon on the decolourisation of the dye aqueous solutions were assessed. In order to analyse the magnitude of external and internal mass transfer resistances, preliminary experiments were carried out at different agitation rates and carbon particle sizes (0.42 mm < ϕ < 2.0 mm and 0.1 mm < ϕ < 0.3 mm). According to this study, a particle size between 0.1 and 0.3 mm was selected, in order to reduce internal mass transfer resistances. The agitation level used was high enough to maintain the system perfectly mixed and without external mass transfer resistances.

The typical reaction tests were performed introducing into the reactor 300 mL of H_2O_2 3 M, 300 mL of a 100-mg L^{-1} dye solution and 1.3 g of activated carbon (0.1 mm < ϕ < 0.3 mm), at the desired pH (adjusted with HCl or NaOH solutions). The effect of the carbon

Table 2
Textural properties of the activated carbon samples

Sample	V_{micro}[a] ($cm^3\,g^{-1}$)	S_{meso}[a] ($m^2\,g^{-1}$)	W_{01}[b] ($cm^3\,g^{-1}$)	W_{02}[b] ($cm^3\,g^{-1}$)	L_1[c] (nm)	S_{BET} ($m^2\,g^{-1}$)
ACo	0.367	125	0.312	0.058	1.1	972
ACa	0.353	91	0.303	0.048	1.1	909
ACb	0.356	114	0.301	0.050	1.2	946

[a] Micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) were calculated by the *t*-method using the standard isotherm proposed by Rodríguez-Reinoso et al. [18].

[b] A type IV deviation was noticed when the N_2 adsorption data was analysed by the Dubinin method [19]; W_{01} and W_{02} are the micropore volumes associated to small and large micropores, respectively.

[c] Average small micropores width (assuming split-shaped geometry) [20].

surface chemistry was examined at an initial pH of 3. The concentrations of dyes in the solutions were determined at appropriate wavelengths (λ_{max}), after recording the respective spectra along time in a JASCO V-560 UV–vis spectrophotometer. This method was used since it was verified that the areas under the curves corresponding to the visible region were proportional to the absorbances at λ_{max}. Previously, the samples were withdrawn from the reaction medium at regular intervals, the reaction was blocked by addition of $Na_2S_2O_3$ [14] and the suspensions were centrifuged.

For comparative purposes, experiments of adsorption on activated carbon and oxidation with H_2O_2 in the absence of activated carbon were also carried out in the reactor described above, under the same conditions.

3. Results and discussion

3.1. Characterization of the activated carbon catalysts

One of the main goals of this work is to study the relationship between the surface chemical characteristics of activated carbons and their performances in the decolourisation of dye solutions. For that purpose, a set of three activated carbon samples (ACo, ACa and ACb) with different levels of acidity/basicity but with no major differences in their textural parameters was considered. The preparation methods of the modified samples ACa and ACb, starting from the commercial ACo, were briefly described in Section 2.1. It is expectable that oxidation with HNO_3 generates an acidic material, due to the introduction of carboxylic acids and anhydrides, lactones and phenol groups [15]. On the other hand, the heat treatment under H_2 atmosphere at high temperatures causes the removal of most of the mentioned surface oxygenated groups, producing basic materials [16]. It is important to notice that the basic characteristics of these materials are not only related to some of the remaining oxygenated groups (e.g. pyrone and chromene type structures), which have Brønsted basic properties, but also to the electron-rich oxygen-free sites on the carbon basal planes (Lewis basicity) [17].

3.1.1. Textural characterization

Table 2 shows the textural parameters of the three materials, calculated from the N_2 adsorption isotherms at 77 K.

As expected, no major differences in the textural properties were noticed. However, a small decrease in the micropore volume and mesopore surface area was observed following the nitric acid treatment, mainly due to the presence of numerous oxygen-containing groups on the surface, which may partially block the access to the pores, and to the possible collapse of some pore walls [21]. The increase of micropore volume and mesopore surface area in sample ACb, relatively to sample ACa, can be explained by the thermal decomposition of some of those oxygenated groups.

Taking into consideration these observations, the eventual different performances of these materials may be primarily attributed to their different chemical surface properties.

3.1.2. Surface chemistry characterization

3.1.2.1. Temperature programmed desorption. Fig. 1 shows the TPD spectra of CO and CO_2 for all the activated carbon samples. TPD is a thermal technique used for the characterization of the oxygen-containing groups present on the activated carbon surfaces. In this technique, the surface groups are thermally decomposed releasing CO and/or CO_2, and in some cases H_2O and H_2, at different temperatures. The nature of each group can be assessed by the decomposition temperature and the type of gas or gases released. The amounts of the various identified groups can be calculated from the areas under the deconvoluted peaks [16,22]. It is well established that CO_2 spectra result from the decomposition of carboxylic acids at low temperatures (<400 °C) and lactones at higher temperatures, while carboxylic anhydrides originate both CO and CO_2. Groups such as phenol, carbonyls, ethers and quinones originate CO peaks at high temperatures [16,22].
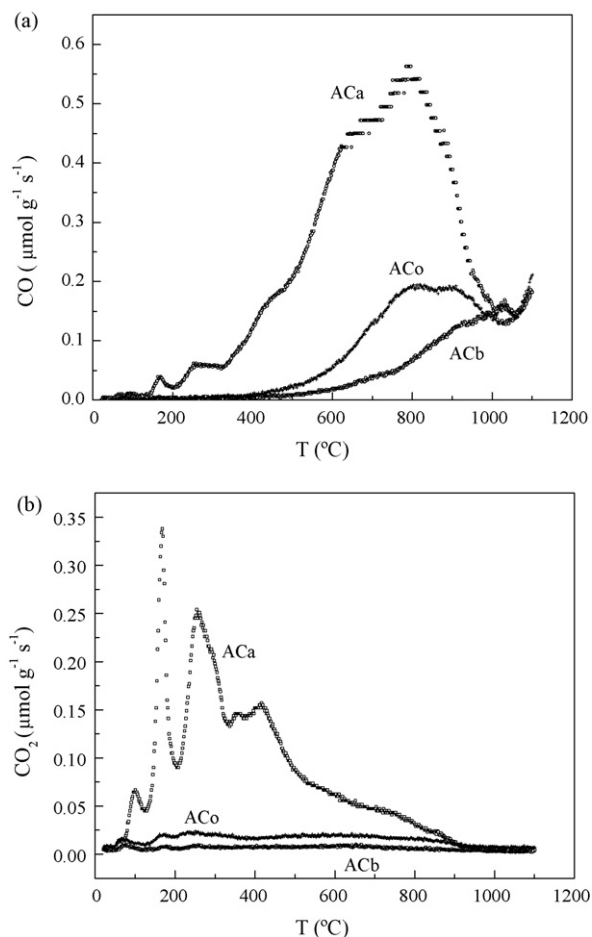

Fig. 1. TPD spectra of the activated carbon samples (heating from room temperature to 1100 °C at 5 °C min^{-1} under helium flow): (a) CO evolution; (b) CO_2 evolution.

Table 3
Selected chemical characteristics of the activated carbon samples

Sample	Acidity (μequiv. g^{-1})	Basicity (μequiv. g^{-1})	pH_{pzc}	CO^a ($\mu mol\,g^{-1}$)	$CO_2{}^a$ ($\mu mol\,g^{-1}$)	CO/CO_2	O^b (% wt.)
ACo	158	318	7.9	995	199	5.0	2.2
ACa	984	27	3.0	2920	964	3.0	7.8
ACb	118	472	9.8	575	83	6.9	1.2

[a] Total amounts of CO and CO_2 released in the TPD experiments per gram of activated carbon.

[b] Mass contents of oxygen (in percentage), calculated from the amounts of CO and CO_2 released per gram of activated carbon.

Taking this into consideration, it can be seen from Fig. 1 that sample ACa, which was oxidised with HNO_3, has the highest amount of surface oxygen-containing groups. These are mainly carboxylic acids, but also considerable amounts of carboxylic anhydrides, lactones, phenol and carbonyl/quinone groups are detected. Since the majority of the mentioned groups has an acid character, obviously this material presents an acid surface.

The thermally treated sample shows completely different TPD spectra. The CO_2 releasing groups were almost completely removed and only a small amount of groups that release CO at high temperatures, most of them of basic nature, remains on the carbon surface. Therefore, it is expected that sample ACb presents basic properties.

3.1.2.2. Acidity, basicity and pH_{pzc}. Table 3 shows the results of acidity, basicity and pH_{pzc} of the activated carbon samples. These results agree with those obtained by TPD. The activated carbon ACa, which has high amounts of oxygen-containing groups (particularly carboxylic groups), presents a surface with the highest acidity and the lowest pH_{pzc} and CO/CO_2 ratio among the studied activated carbons. On the other hand, the thermal treatment produces a material (ACb) with a strong basic character (high basicity, high pH_{pzc} and high CO/CO_2 ratio). As already mentioned, in addition to the Brønsted basicity that results from some remaining oxygen-containing surface groups (e.g. pyrone and chromene type structures), also the oxygen-free Lewis basic sites on the graphene layers must be considered [17]. Finally, it may be observed that the starting commercial activated carbon ACo has a slightly basic nature.

3.2. Decolourisation of dye aqueous solutions

The decolourisation of the selected dye solutions at an initial concentration of $50\,mg\,L^{-1}$ was carried out by three processes: adsorption on activated carbon and oxidation with H_2O_2 in the presence or absence of activated carbon. The effects of different reaction conditions such as the initial pH of the solution and the surface chemistry of the activated carbon were evaluated.

In order to simplify the discussion, the presentation of results will be divided in terms of the dyes studied, considering in the first place those analysed with more detail, namely the dyes CI Reactive Red 241 and CI Acid Blue 113. In the end, some remarks about the results obtained with the other selected dyes are included.

3.2.1. CI Reactive Red 241

The decolourisation kinetic data obtained with the solutions of this reactive dye are depicted in Figs. 2 and 3. In the former, the influence of the activated carbon surface chemistry can be evaluated, while the latter is mainly related to the relative importance of the solution pH on the performance of the process.

It is not our goal to present a detailed kinetic analysis; however, it was possible to fit the curves using first or second-order models, respectively according to the well-known expressions:
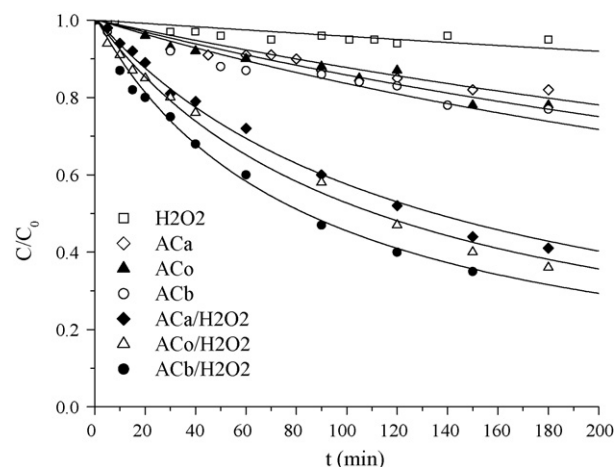
$$\frac{C}{C_0} = \exp(-k_1\,t) \tag{1}$$

Fig. 2. Normalized colour retained in the CI Reactive Red 241 solution ($C_0 = 50\,mg\,L^{-1}$) at acid conditions (pH 3) by non-catalytic oxidation (H_2O_2), and adsorption (ACx) or catalytic oxidation (ACx/H_2O_2) in the presence of the activated carbon samples ($m_{AC} = 1.3\,g$). Other experimental conditions: $V_{solution} = 600\,mL$; $[H_2O_2]_0 = 1.5\,M$.

$$\frac{C}{C_0} = \frac{1}{1 + k_2 C_0 t} = \frac{1}{1 + k_2^*\,t} \tag{2}$$

where C and C_0 are the concentrations of dye, respectively at time t and in the beginning of the kinetic experiment, and k_1 and k_2^* the pseudo-rate constants associated to the two models. The corresponding results are presented in Table 4. Both models are reasonably accurate, although the second-order kinetics seems a little better. It is also important to notice that the three curves shown in
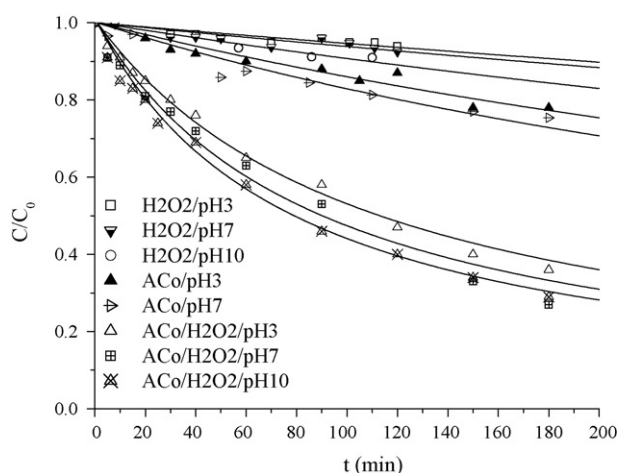

Fig. 3. Effect of pH on the normalized colour retained in the CI Reactive Red 241 solution by non-catalytic oxidation (H_2O_2/pHx), adsorption on the commercial activated carbon (ACo/pHx) and catalytic oxidation in the presence of the same activated carbon sample (ACo/H_2O_2/pHx). Experimental conditions: $C_0 = 50\,mg\,L^{-1}$; $m_{AC} = 1.3\,g$; $V_{solution} = 600\,mL$; $[H_2O_2]_0 = 1.5\,M$.

Table 4
Kinetic parameters for the curves in Figs. 2 and 3

	First-order		Second-order	
	k_1 (min^{-1})	R^2	k_2^* (min^{-1})	R^2
H$_2$O$_2$[a]	$(4.2 \pm 0.5) \times 10^{-4}$	0.416	$(4.4 \pm 0.5) \times 10^{-4}$	0.439
ACa[a]	$(1.29 \pm 0.07) \times 10^{-3}$	0.912	$(1.41 \pm 0.07) \times 10^{-3}$	0.934
ACo[a]	$(1.53 \pm 0.09) \times 10^{-3}$	0.908	$(1.7 \pm 0.1) \times 10^{-3}$	0.915
ACb[a]	$(1.8 \pm 0.1) \times 10^{-3}$	0.900	$(2.0 \pm 0.1) \times 10^{-3}$	0.917
ACa/H$_2$O$_2$[a]	$(5.4 \pm 0.1) \times 10^{-3}$	0.993	$(7.4 \pm 0.2) \times 10^{-3}$	0.992
ACo/H$_2$O$_2$[a]	$(6.2 \pm 0.2) \times 10^{-3}$	0.987	$(9.1 \pm 0.3) \times 10^{-3}$	0.994
ACb/H$_2$O$_2$[a]	$(8.7 \pm 0.4) \times 10^{-3}$	0.964	$(1.21 \pm 0.04) \times 10^{-2}$	0.993
H$_2$O$_2$/pH 3[b]	$(5.5 \pm 0.5) \times 10^{-4}$	0.757	$(5.7 \pm 0.5) \times 10^{-4}$	0.767
H$_2$O$_2$/pH 7[b]	$(6.4 \pm 0.7) \times 10^{-4}$	0.688	$(6.6 \pm 0.7) \times 10^{-4}$	0.699
H$_2$O$_2$/pH 10[b]	$(9.8 \pm 0.7) \times 10^{-4}$	0.941	$(1.03 \pm 0.08) \times 10^{-3}$	0.948
ACo/pH 3[b]	$(1.48 \pm 0.08) \times 10^{-3}$	0.928	$(1.64 \pm 0.09) \times 10^{-3}$	0.937
ACo/pH 7[b]	$(1.8 \pm 0.1) \times 10^{-3}$	0.914	$(2.1 \pm 0.1) \times 10^{-3}$	0.941
ACo/H$_2$O$_2$/pH 3[b]	$(6.5 \pm 0.2) \times 10^{-3}$	0.984	$(8.9 \pm 0.3) \times 10^{-3}$	0.993
ACo/H$_2$O$_2$/pH 7[b]	$(7.6 \pm 0.3) \times 10^{-3}$	0.984	$(1.12 \pm 0.07) \times 10^{-2}$	0.981
ACo/H$_2$O$_2$/pH 10[b]	$(9.1 \pm 0.6) \times 10^{-3}$	0.951	$(1.28 \pm 0.05) \times 10^{-2}$	0.989

[a] Experimental curves in Fig. 2.
[b] Experimental curves in Fig. 3.

Fig. 3 for pH 3 (non-catalytic oxidation, adsorption and oxidation in the presence of the commercial activated carbon) are duplicates of the corresponding curves in Fig. 2; the comparison between the respective curves and/or pseudo-rate constants in Table 4 allows to conclude that the experimental results are reproducible.

Fig. 2 shows the effect of the activated carbon chemical surface properties on the kinetics of decolourisation by adsorption and promoted oxidation. The oxidation with H$_2$O$_2$ in the absence of activated carbon is not significant, particularly at low pH, as is the case. Adsorption on activated carbon is a process that also presents a low performance for colour removal from solutions of this type of dye, because of its high molecular size and relatively low affinity to the surface of activated carbon, for instance comparatively with basic or acid dyes [9]. Nevertheless, there is a significant cooperative effect when oxidation is carried out in the presence of activated carbon. In fact, for example, the colour removal after 3 h increases from 22% in the adsorption on the original activated carbon to 64% in the oxidation promoted by the same sample.

After observing the positive effect of the simultaneous use of H$_2$O$_2$ and activated carbon, it is also evident that the surface chemistry of the catalyst has a significant effect in the efficiency of this type of advanced oxidation process. As can be seen in Fig. 2, there is a close relationship between the rate of colour removal by adsorption or catalytic oxidation and the basicity of the sample used. The dye uptake by adsorption increases with the basicity of the activated carbon. This behaviour was already discussed in detail in some previous publications of our team [8,9,23]. Briefly, the adsorption of the reactive dye mainly involves dispersive interactions between the delocalized π electrons on the carbon basal planes and the free electrons in the dye molecules (e.g. in the aromatic rings). Since the presence of electron-withdrawing oxygenated groups on the carbon surface is unfavourable for the process, sample ACb has the highest adsorption capacity. Additionally, at pH 3, ACb and ACo surfaces are positively charged (see pH$_{pzc}$ values in Table 3), and therefore adsorption on these samples may be enhanced via electrostatic attractions, taking into account the anionic nature of the reactive dye in solution.

It is evident that the correlation between performance and carbon basicity is even more significant in the advanced oxidation process. Activated carbon catalyses the decomposition of hydrogen peroxide into free radicals, such as hydroxyl radicals, which are very active in oxidation reactions in the aqueous phase [24]. The electron transfer from the surface of activated carbon seems to be involved in the corresponding mechanism, accordingly to a pathway similar to the Fenton reaction [13]:

$$AC + H_2O_2 \rightarrow AC^+ + HO^- + HO^\bullet \qquad (3)$$

$$AC^+ + H_2O_2 \rightarrow AC + HO_2^\bullet + H^+ \qquad (4)$$
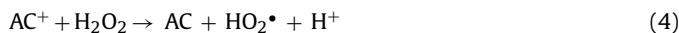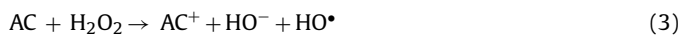
where AC and AC$^+$ represent the reduced and the oxidized catalyst states, respectively. Similarly to what was observed in other studies [12,25], this mechanism is consistent with the enhanced activity of basic activated carbons, since the free electrons on the graphene basal planes of activated carbon (corresponding to Lewis basicity) participate in it. As most of the oxygenated groups abundantly present on the surface of acidic samples have an electron withdrawn capacity, the electron transfer process necessary for the decomposition of hydrogen peroxide into highly reactive radicals (Eq. (3)) is reduced, which explains why sample ACa presents the lowest catalytic activity.

The effect of initial pH may be discussed on the basis of data presented in Fig. 3. First, it is clear that colour removal in the absence of activated carbon is not significant, particularly at pH 3 and 7. The incipient decolourisation observed in these conditions results from the direct attack of H$_2$O$_2$ on the dye molecules. At pH 10 this non-catalysed oxidation is favoured, although the decolourisation level is also insufficient for practical purposes (only about 10% after 2 h). Considering that hydrogen peroxide is a weak acid with pK_a = 11.6, this behaviour may be explained by the formation of the perhydroxyl anion HO$_2^-$ in basic conditions (H$_2$O$_2 \leftrightarrows$ H$^+$ + HO$_2^-$), since it is known that this anion is a strong oxidizing agent [26]. In a recent publication, other authors also considered the occurrence of the mentioned anion as responsible for the enhancement of the oxidative decolourisation of CI Direct Green 28 by hydrogen peroxide in alkaline media [27].

Considering the adsorption data in Fig. 3, it can be observed that the solution pH has not a major effect in the kinetics of decolourisation. In a previous work [23], where the influence of pH on the surface charge of the adsorbent and the electrostatic interactions referred above were assessed, it was concluded that the pH value must be lower than the pH$_{pzc}$ of the activated carbon in order to maximize adsorption. Actually, it was experimentally shown by Órfão et al. [23] that the equilibrium uptake of CI Reactive Red 241 on a commercial activated carbon, similar to that used in the present study, is favoured when the solution is strongly acid. Nevertheless, it was also observed that no significant differences in the adsorption kinetic curves were obtained for low initial dye

concentrations ($\leq 100\,\mathrm{mg\,L^{-1}}$), as is the case in the present study ($C_0 = 50\,\mathrm{mg\,L^{-1}}$).

Even considering the dye oxidation rate by direct reaction, which is limited but increases from pH 3 to 10 as discussed before, there is also a similar but more significant effect of the solution pH in the activated carbon promoted decolourisation (see pseudo-rate constant values in Table 4 and curves in Fig. 3). A possible explanation for this behaviour is related to the surface chemical characteristics of activated carbons. When pH < $\mathrm{pH_{pzc}}$, activated carbons develop a positive surface charge, since the electron-rich zones in the graphene layers, which act as Lewis basic centres, accept protons from the aqueous solution [28]. As these electrons participate in the mechanism of hydroxyl radical formation (Eqs. (3) and (4)), this may explain the observed relative activities: pH 3 < pH 7 < pH 10 ($\mathrm{pH_{pzc}}$ = 7.9 for sample ACo, as shown in Table 3).

It is predictable that some chemical modifications of the activated carbon may occur during reaction, since some additional oxygenated groups may be formed on the surface of activated carbon as a result of the prolonged contact with H_2O_2 [29]. In order to verify this possibility, the activated carbon sample ACo, after being used in the catalytic experiment at pH 7, was removed from the liquid at the end of the respective test (about 3 h), dried in an oven, and analysed by TPD and XPS. It was verified by TPD that the CO and CO_2 spectra were not significantly different from those corresponding to the original sample. The calculated mass content of oxygen was 2.3%, which is only slightly higher than the value of 2.2% obtained with the same sample before reaction (cf. with Table 3); this result is in agreement with our previous observations [8]. It is important to notice that the present hydrogen peroxide concentration is much lower than the concentration of 9.8 M used by Moreno-Castilla et al. [29]. On the other hand, XPS results indicate that the percentage of oxygen approximately doubles after reaction. This is not surprising, since this technique provides an evaluation of the chemical composition corresponding to the few uppermost layers of the material (2–5 nm), which are more easily oxidised, while by the TPD spectra it is possible to calculate the overall oxygen content of the sample. It is possible to conclude that the scarce introduction of oxygen-containing groups during reaction can slightly deactivated the catalyst, but this is not too much significant, mainly considering that the acid activated carbon ACa is active.

3.2.2. CI Acid Blue 113

The results obtained with the acid dye are depicted in Fig. 4. Although practically no decolourisation was achieved at pH 3 in the absence of activated carbon, a colour removal of approximately 20% was achieved at pH 7 after 3 h. This indicates that this dye is more susceptible to the direct attack of hydrogen peroxide than CI Reactive Red 241. Considering the adsorption data, it can be concluded that this acid dye has a stronger affinity towards the surface of the activated carbon samples than the reactive dye, which agrees with our previous observations [9]. Once again, there is an evident influence of the surface chemistry on the adsorption performance, particularly comparing the decolourisation levels obtained with samples ACa and ACo. As the acid dye is also anionic, the explanation for this behaviour is the same as that considered in the previous section and, as discussed there, it is based on the involvement of π–π dispersive and electrostatic interactions in the adsorption phenomenon.

The efficiency of the decolourisation at pH 3 in the presence of the three activated carbon samples follows the same trend as in the case of the reactive dye treated in the previous section (ACa < ACo < ACb), but the comparison between the corresponding results and those obtained by activated carbon adsorption allows to conclude that the improvement attained with sample ACa is higher
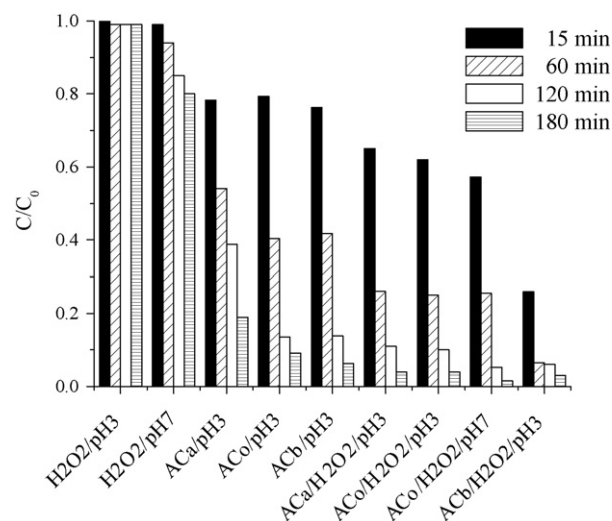

Fig. 4. Normalized colour retained in the CI Acid Blue 113 solution by non-catalytic oxidation (H_2O_2/pHx), adsorption (ACx/pH3) and catalytic oxidation (ACx/H_2O_2/pHx), after the operational times indicated. Experimental conditions: $C_0 = 50\,\mathrm{mg\,L^{-1}}$; $m_{AC} = 1.3\,\mathrm{g}$; $V_{solution} = 600\,\mathrm{mL}$; $[H_2O_2]_0 = 1.5\,\mathrm{M}$.

than with sample ACo. To explain these results it is important to notice that dye and H_2O_2 species compete for the same active sites on the catalyst surface (mainly, the free electrons in the graphene basal planes) [30]. Then, in relative terms, the lower dye adsorption uptake on the sample ACa seems to be favourable to the catalytic mechanism. In order to better understand this explanation, it is essential to mention, according to Georgi and Kopinke [13] that the hydroxyl radicals formed react with the organic molecules in the liquid phase, being the adsorbed species nearly unreactive. Nevertheless, sample ACb is the most active, since the number of oxygenated surface groups is very low and, therefore, the concentration of active sites available seems to be sufficiently high to promote radicals formation very efficiently, even when part of the surface is occupied by dye species.

Finally, the experiment carried out at a different value of pH (pH 7) indicates that the effect of this parameter is not as significant as in the decolourisation of the reactive dye described in the previous section, at least in the pH range 3–7. Probably, the slight enhancement of colour removal at pH 7 relatively to pH 3 must be ascribed to the non-catalytic peroxidation.

3.2.3. Other dyes

The decolourisation of other dyes in aqueous solutions at pH 7 was assessed for adsorption and non-catalytic or catalytic oxidation, using the commercial activated carbon ACo.

For example, the dye CI Reactive Blue 5 was only relatively decolourised by adsorption (approximately 40% removal after 3 h). Then, a significant cooperative effect between H_2O_2 and activated carbon, of the type described in the two previous sections, was observed.

On the contrary, the redox indicator methylene blue and the textile dye CI Acid Yellow 49 shown a high affinity to the activated carbon, i.e. the colour removal efficiencies by adsorption were high enough to prevent any significant catalytic effect of the activated carbon, in agreement with the reasoning presented before.

In all cases described until now, the decolourisation with hydrogen peroxide in the absence of activated carbon is only residual or even non-existent. The only observed exception arose when the dye CI Basic Red 14 was evaluated. With this dye, a 100% colour removal was attained after 30 min just adding H_2O_2 to the solution, a performance even better than that obtained by adsorption

on the activated carbon. Of course, the catalytic effect of activated carbon in the peroxide decolourisation of this solution was only marginal.

These examples and those treated in the two previous sections show that activated carbon may catalyse the degradation of dyes with hydrogen peroxide, providing that adsorption or simple direct peroxidation are not too much effective.

4. Conclusions

A systematic approach was followed in order to evaluate the decolourisation efficiency of dye aqueous solutions by reaction with hydrogen peroxide in the presence of activated carbon as catalyst. Special attention was given to the importance of the solution pH and to the chemical characteristics of the catalyst. In this scope, three activated carbon samples, mainly differing in the respective surface chemistries, were prepared and characterized.

The experimental results were essentially interpreted on the basis of a generally accepted mechanism, which involves the formation of hydroxyl radicals on the catalyst surface. The interactions of dyes species and H_2O_2 molecules with the activated carbons were also considered and discussed.

For some of the dyes analysed, non-catalytic peroxide oxidation or adsorption on activated carbon are processes highly effective for colour removal. Obviously, in these cases, the cooperative action of activated carbon and H_2O_2 in decolourisation is only marginal or even non-existent.

However, particularly considering the reactive dyes, which generally present a low affinity to carbon surfaces and only residual direct reactivity with hydrogen peroxide, a significant synergic effect may be attained when carrying out the oxidation in the presence of activated carbon. This is due to the capability of activated carbon to catalyse the formation of hydroxyl radicals, which are very reactive.

In these circumstances, it was proved that basic activated carbons and neutral or basic solutions are favourable for the catalytic process. This is an additional advantage relatively to the well-known Fenton process, which is carried out at low pH, although the later is generally more efficient.

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