

Activated carbons treated with sulphuric acid: catalysts for catalytic wet peroxide oxidation

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Abstract

The commercial activated carbon Norit ROX 0.8 was subjected to different liquid phase treatments in order to produce activated carbons with varying surface chemistry and acid/base character. The prepared materials were used as catalysts in the catalytic wet peroxide oxidation of the acid dye Chromotrope 2R in order to assess their removal activity. Chemical characterization of the prepared materials includes determination of the point of zero charge and evaluation of the concentration and nature of acidic and basic surface functionalities by acid/base titrations and temperature programmed desorption. The relationship between the surface chemistry and efficiency for dye removal is discussed. In general, dye removal is increased when using catalysts with higher basic character, due to enhanced electrostatic attraction between the acid dye and the catalyst surface when compared with catalysts presenting acidic character. In addition, treatment with sulphuric acid introduces on the catalysts surface sulphur containing groups, which promotes the surface interaction between the pollutant and hydrogen peroxide. This leads to improved dye removal resulting from higher production of hydroxyl radicals close to the pollutant. Reutilization studies show that the catalyst prepared by sulphuric acid treatment is able to keep its performance in successive runs.

Key Words : Activated carbon; Surface chemistry; Sulphur containing functional groups; Catalytic wet peroxide oxidation

1 Introduction

The Fenton process is widely recognized as a low cost Advanced Oxidation Process, able to operate at atmospheric pressure and room temperature with a simple technology [1]. The high efficiency in the degradation of organic pollutants is due to the participation of hydroxyl radicals, very reactive oxidizing species resulting from the catalytic decomposition of hydrogen peroxide in presence of Fe(II). However, to avoid the existence of iron in the treated waters, additional separation steps are needed to remove it. Trying to solve this drawback, several efforts have been done to develop iron containing heterogeneous catalysts to promote the generation of the desired hydroxyl radicals [1]. Many of the developed catalysts frequently show stability problems under the process operating conditions due to iron leaching. A strategy to completely eliminate the presence of iron in the treated waters passes through the development of heterogeneous catalysts with no metallic phase, but with the adequate ability to promote the formation of the oxidizing agent. Recent results show that activated carbons are active in the degradation of some dissolved organic pollutants in the presence of hydrogen peroxide [2, 3], providing that they possess suitable chemical surface properties. Activated carbons are known catalysts for hydrogen peroxide decomposition through the formation of hydroxyl radicals. Therefore, it seems logical to use these radicals in the degradation of organic pollutants adsorbed and concentrated over activated carbons.

In this work we studied the influence of activated carbons surface chemistry on the efficiency of catalytic wet peroxide oxidation of the azo dye Chromotrope 2R (C2R). This dye was selected as model pollutant, since the removal of colour from textile effluents has been an issue of very active research in the field of wastewater treatment, due to the high environmental and social concerns associated with this type of pollution.

2 Experimental section

2.1 Catalysts preparation

Four different activated carbons were used as catalysts in this work: the activated carbon Norit ROX 0.8 (AC), as it is, and chemically modified by liquid phase treatments with nitric acid (ACNA), hydrogen peroxide (ACHP) and sulphuric acid (ACSA). Nitric acid oxidation was carried out boiling 10 g of AC in 200 mL of 5 M nitric acid solution for 3 h. The treatment with hydrogen peroxide was performed wetting 10 g of AC with 200 mL of hydrogen peroxide solution 30 wt.% at room temperature for 24 h. In sulphuric acid oxidation 10 g of AC were immersed in 200 mL of 5 M acid solution for 3 h at 353 K. After the liquid phase treatments, all samples were thoroughly washed with distilled water until the neutrality of the rinsing waters and further dried in oven for 18 h at 383 K.

2.2 Catalysts characterization

The surface chemistry of the carbon materials was characterized by (i) their point of zero charge (PZC), determined by mass titration [4]; (ii) the concentration of acidic and basic sites, using titration techniques [5] and (iii) the nature of the oxygen containing groups on the materials surface, identified by temperature programmed desorption (TPD). TPD analysis was performed in a fully automated AMI-200 Catalyst Characterization Instrument (Altamira Instruments), equipped with a quadrupole mass spectrometer (Dymaxion, Ametek). The catalyst sample (0.10 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5 K.min⁻¹ up to 1373 K using a constant flow rate of helium (25 cm³.min⁻¹, STP). The mass signals 28, 44, 48 and 64 amu were monitored during the thermal analysis, the corresponding TPD spectra being obtained.

2.3 Catalytic runs

The oxidation experiments of 100 mg.L⁻¹ Chromotrope 2R aqueous solutions were performed at 50°C and initial pH adjusted to 3, with 0.5 g.L⁻¹ of catalyst and 34.6 mM of hydrogen peroxide (corresponding to approximately 5 times the stoichiometric amount needed to completely mineralize C2R). In order to assess the contribution of adsorption on the removal of the pollutant, blank experiments were performed under the same operating conditions without added hydrogen peroxide. Small aliquots were periodically withdrawn from the reactor to be further analyzed in terms of azo dye concentration, determined by UV-vis spectrophotometry. The hydrogen peroxide concentration in decomposition experiments was monitored by permanganometry.

3 Results and discussion

3.1 Catalysts characterization

The acid/base character of the tested materials, determined by PZC measurements and by acid/base titrations, is shown in Table 1.

Table 1: Point of zero charge, concentration of acidic and basic active sites and concentration of CO, CO₂, SO and SO₂ released during TPD of the carbon materials subjected to different liquid phase treatments

| Catalyst | PZC (± 0.1) | Acidity (± 10 µmol.g ⁻¹) | Basicity (± 10 µmol.g ⁻¹) | CO (± 20 µmol.g ⁻¹) | CO ₂ (± 20 µmol.g ⁻¹) | SO (± 1 a.u.) | SO ₂ (± 1 a.u.) |
|----------|----------------|---|--|------------------------------------|---|------------------|-------------------------------|
| AC | 7.6 | 270 | 540 | 1200 | 380 | 15 | 41 |
| ACHP | 6.8 | 390 | 510 | 1560 | 480 | 14 | 40 |
| ACSA | 5.8 | 800 | 300 | 1360 | 420 | 84 | 200 |
| ACNA | 2.0 | 840 | 110 | 5140 | 3040 | 4 | 0 |

The original AC possesses an evident basic character, with twice the concentration of basic functionalities ($540 \mu\text{mol.g}^{-1}$) in comparison to acidic functionalities ($270 \mu\text{mol.g}^{-1}$). While the treatment of AC with hydrogen peroxide resulted in a material with a slightly less basic character, the treatment with sulphuric acid produced a material with a markedly acid character, the concentration of acidic surface groups ($800 \mu\text{mol.g}^{-1}$) being found to be 2.7 times higher than the concentration of basic surface groups ($300 \mu\text{mol.g}^{-1}$). When nitric acid was used, the acidic character of the obtained material was even stronger, with the concentration of acidic surface groups ($840 \mu\text{mol.g}^{-1}$) found to be 7.6 times higher than the concentration of basic surface groups ($110 \mu\text{mol.g}^{-1}$). The PZC values of all materials are in accordance with their acid/base properties, lower PZC corresponding to higher acidic character.

The TPD spectra of CO, CO₂, SO and SO₂ are shown in Figure 1 and the concentration of the monitored species are gathered in Table 1, allowing to identify the nature of the functional groups introduced on the surface of the carbon samples subjected to the different liquid phase treatments.

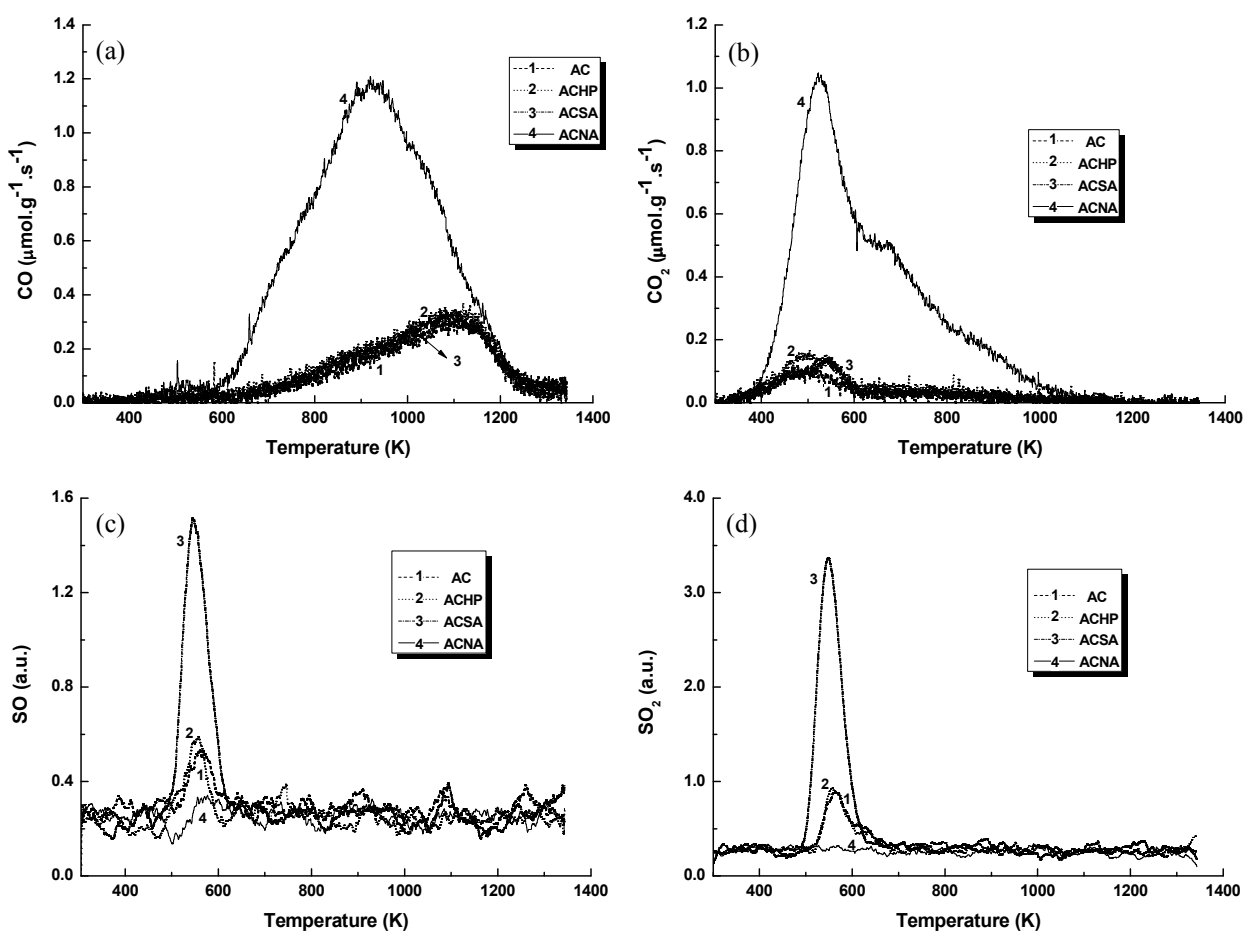


Figure 1. TPD spectra of the carbon materials subjected to different liquid phase treatments: (a) CO, (b) CO₂, (c) SO and (d) SO₂ evolution

From the observation of the CO and CO₂ spectra it is clear that the thermal decomposition of ACNA results in a much higher release of CO and CO₂ species, when compared with the original AC. The concentration of the evolved CO and CO₂ increased from 1200 and 380 $\mu\text{mol.g}^{-1}$, respectively, for the AC, to 5140 and 3040 $\mu\text{mol.g}^{-1}$, for the ACNA. This strong increase in the concentration of functional groups upon nitric acid oxidation is mainly attributed to the presence of large amounts of surface acidic carboxylic groups (CO₂ peak maxima 510-720 K) and phenols (CO peak maxima 900-990 K) on the material [6]. The introduction of functional groups decomposing as CO and CO₂ at the surface of the materials ACHP and ACSA is rather modest. This is in agreement with the slight increase of the ACHP acidity (when compared with AC), but not with the significant increase of ACSA acidity (Table 1). Following the SO and SO₂ concentration development in the

TPD spectra, it is clear the release of these groups on ACSA when compared with the other materials. The peak area of SO and SO₂ increased from 15 and 41, respectively, in the AC, to 84 and 200, in the ACSA. This is mainly due to the introduction of thiol and sulphonic acid groups at the surface upon sulphuric acid treatment, which decomposes releasing SO and SO₂ species [7]. It is worth note that the original AC possesses a non-negligible concentration of sulphur containing surface groups, which are removed by the nitric acid treatment but not affected by the hydrogen peroxide. In summary, the differences observed in the acid/base characteristics given in Table 1 are mainly due to the increase in the concentration of carboxylic acid and phenol groups in the ACNA material and to the increase in the concentration of sulphur containing groups in the ACSA.

3.2 Catalytic wet peroxide oxidation

The C2R removal results obtained with the tested activated carbon materials, either in the adsorption and reaction experiments, are given in Figure 2.

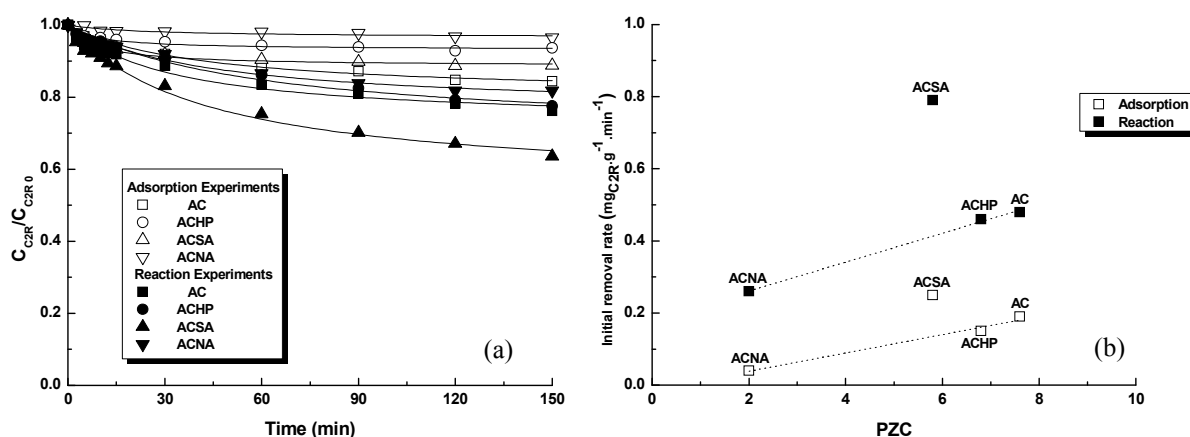


Figure 2. Results obtained for the removal of C2R in adsorption and reaction experiments at 323 K (a) concentration decay curves; (b) initial removal rates against carbon sample PZC values

From Figure 2(a), it is observed that the contribution of adsorption in the removal of C2R is not negligible and that depends on the carbon sample used, more specifically on their surface chemistry, since their textural properties were found to be similar ($S_{BET} \approx 850 \text{ m}^2.\text{g}^{-1}$). For each carbon sample it is observed that the introduction of hydrogen peroxide in the system clearly increases C2R removal due to reaction. This effect is particularly noticeable for the ACSA. The initial C2R adsorption and reaction removal rates, defined as mass of C2R removed per minute and per mass of adsorbent or catalyst are plotted against the corresponding PZC values in Figure 2(b). Also here there is a relationship between the surface chemistry and both initial adsorption and reaction rates.

The initial adsorption rates ($\text{mg}_{C2R}.\text{g}^{-1}.\text{min}^{-1}$) change from 0.04 to 0.25, for ACNA and ACSA samples, respectively. The low adsorption performance of ACNA is related to its PZC value (2.0) and to the fact that C2R in solution is found in an anionic form. Since PZC is lower than the solution pH of 3, the carbon surface will be negatively charged and the anionic dye will suffer repulsion forces when close to the activated carbon surface, thus inhibiting adsorption [8]. When the PZC is higher than the solution pH, the surface of activated carbon will be positively charged, favouring the adsorption of the anionic dye by electrostatic attraction [8]. The influence of PZC of activated carbons in the adsorption of anionic and cationic dyes is well documented in the literature [9]. In the case of anionic dyes in solutions at pH = 3, adsorption normally increases with increasing PZC. The same behaviour is observed in our adsorption results, except for ACSA (Figure 2(b)). The nature of groups introduced at the carbon surface when treated with sulphuric acid is rather different than those introduced upon the other conventional treatments (hydrogen peroxide treatment and nitric acid oxidation), thiol, sulphonic acid, sulfoxides and/or sulphone and sulphide groups prevailing over carboxylic acid, carboxylic anhydrides, lactones, phenol and quinone groups [7]. The higher initial adsorption rate observed when using the sample treated with sulphuric acid may then be explained in terms of the presence of sulphur containing groups on the surface. It is

noticeable to observe that adsorption contributes to 1/3 of the total removal rates in oxidizing conditions.

Regarding the reaction experiments, the highest initial reaction rate was obtained with ACSA ($0.79 \text{ mg}_{\text{C2R}} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$), while the lowest was obtained with ACNA ($0.26 \text{ mg}_{\text{C2R}} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$). Once again, there is a correlation between C2R removal rates and the acidic nature of the activated carbons (Figure 2(b)), which is distorted by the presence of sulphur containing functional groups, which seem to play an important role in pollutant removal. This may be due to the hydrophilic character of these groups, which enable a more intimate contact between the aqueous solution and the ACSA carbon surface, thus increasing the corresponding adsorption of C2R and hydrogen peroxide molecules, essential steps for further reaction of C2R with hydroxyl radicals generated at the catalyst surface. In order to evaluate the activity of each carbon sample for the decomposition of hydrogen peroxide, decomposition experiments were carried out under the same conditions described in the experimental section, but without added C2R. The results are shown in Figure 3, evidencing that the decomposition of hydrogen peroxide is strongly influenced by the carbon catalyst used, and consequently, by their surface chemistry. Since the decomposition of hydrogen peroxide involves the generation of hydroxyl radicals, an efficient catalyst is the one showing simultaneously high activity for hydrogen peroxide decomposition and for the reaction between generated hydroxyl radicals and adsorbed pollutant. It is noticeable that the activity of the tested catalysts for hydrogen decomposition increases fairly in the same order as the activity found previously for C2R removal, i.e., $\text{ACSA} > \text{AC} > \text{ACHP} > \text{ACNA}$, thus allowing to conclude that nitric acid and hydrogen peroxide treatments decrease the activity of the original AC while the presence of sulphur containing groups on the surface of the carbon samples will slightly benefit the reaction (as shown in Figure 3). In addition, the activated carbon treated with sulphuric acid increases the efficiency of the reaction between the generated hydroxyl radicals and adsorbed C2R (as inferred from Figure 2).

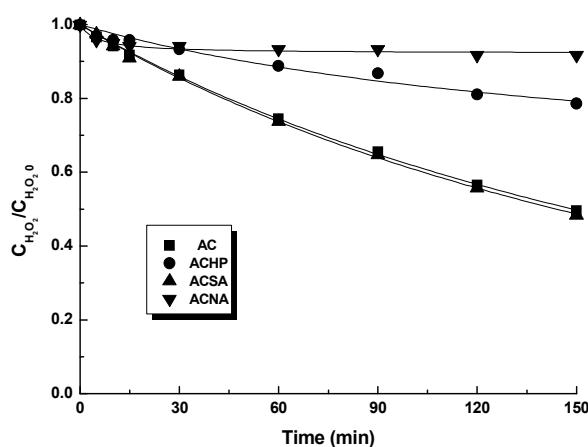


Figure 3. Hydrogen peroxide decomposition experiments at 323 K over carbon catalysts with varying surface chemistry

The capacity of ACSA to be used in continuous experiments was assessed by reutilization studies. After an oxidation run, the catalyst was recovered from the solution, washed with water until neutrality of the rinsing waters and dried in oven at 383 K for 18 h. The recovered catalyst was then used in a new experiment with fresh reactants under the same conditions described for the first run in the experimental section. The recovery procedure was repeated until the original ACSA catalyst was used four times. The results obtained are shown in Figure 4, in terms of initial reaction rate. It is observed that the highest initial reaction rate was achieved with the fresh catalyst ($0.79 \text{ mg}_{\text{C2R}} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$). There was a 25% decrease of the rate for the second run, which then remained constant around $0.59 \text{ mg}_{\text{C2R}} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ for the subsequent runs (up to four). If we take into consideration that, in the first run, adsorption contributes with 1/3 to the total C2R removal, the loss of removal activity from the first to the following runs may be explained by adsorption of organic matter at the surface of ACSA, which was not completely desorbed after the reconditioning of the catalyst. Then, at the beginning of the second run, the catalyst surface already contains some

adsorbed pollutant, thus the initial removal of C2R due to adsorption does not occur in the same extent as in the first run. Therefore, the observed removal is mainly due to adsorbed C2R degradation by reaction with hydroxyl radicals generated on the catalyst surface from the decomposition of adsorbed hydrogen peroxide.

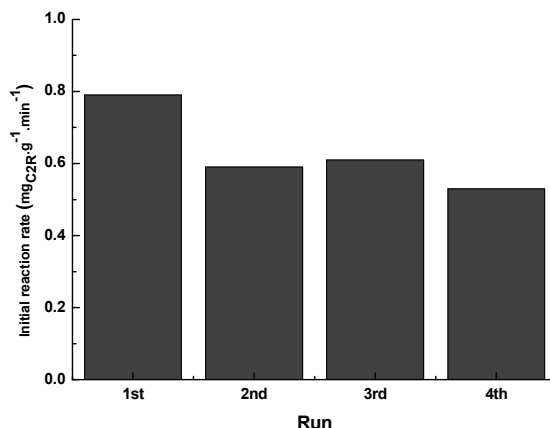


Figure 4. Reaction results obtained for the removal of C2R in reutilization experiments at 323 K using ACSA

4 Conclusions

Activated carbons treated with sulphuric acid show an unexpected efficiency in catalytic wet peroxide oxidation processes. When conventional treatments are used to modify the surface chemistry, the removal of a model anionic dye is mainly governed by the acid/base character of the carbon surface, higher basic character favouring the efficiency of the catalyst. When surface groups containing sulphur are introduced, the removal of the molecule is enhanced due to greater affinity between the reactants and the catalyst surface, favouring the generation of very reactive hydroxyl radicals in the vicinity of the pollutant. Reutilization studies show that the catalyst prepared by sulphuric acid treatment is able to keep its performance in successive runs.

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6 References

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