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

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ABSTRACT

Different liquid phase thermal treatments were applied to a commercial activated carbon (Norit ROX 0.8) in order to produce modified activated carbons with varying surface chemistry and increased acidic character. 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 prepared materials were used as catalysts in the catalytic wet peroxide oxidation of the acid dye Chromotrope 2R in order to assess their removal efficiency. The relationship between the surface chemistry and efficiency for dye removal is discussed. As expected, decreasing acidity of the catalysts surface will correlate with increasing dye conversion. Unexpectedly, treatment with sulphuric acid leads to a very high yield of dye removal which falls out of the previous correlation. This was explained in terms of the introduction of sulphur containing groups on the carbon surface, which promotes the surface interaction between the pollutant and hydrogen peroxide: higher production of hydroxyl radicals close to the pollutant leads to improved dye removal. In addition, reutilization studies show that the catalyst prepared by sulphuric acid treatment is able to keep its performance in successive runs.

## 1. Introduction

The research and development of efficient wastewater treatment technologies received in recent years great attention from the scientific community, especially in the case of the so called advanced oxidation processes (AOP) [1,2]. Among all the possibilities, the Fenton process is widely recognized as a low cost AOP, able to operate at atmospheric pressure and room temperature with a simple technology [3,4]. 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 the presence of Fe(II). However, due to transference of the iron into the treated waters, additional separation steps are needed to remove it. To solve this drawback, several efforts have been done to develop heterogeneous catalysts containing non-leaching iron, which will be able to generate the desired hydroxyl radicals [5–9]. Nevertheless, the problem still remains, since many of these developed catalysts are barely stable and do leach under process operating conditions. An alternative strategy is to completely eliminate the presence of iron through the use 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 efficient in the degradation of some dissolved organic pollutants in the presence of hydrogen peroxide [10–13], providing that the carbon surface possesses suitable chemical 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.

Activated carbons, and carbon materials in general, are very flexible materials, since their textural and surface chemical properties can be easily tuned by proper chemical and physical treatments [14,15]. Those properties have been thoroughly studied by our group in order to produce suitable catalytic materials for a wide range of specific applications, in particular activated carbons, carbon xerogels and carbon nanotubes for catalytic wet air oxidation [16–18].

When conventional treatments are used to modify the surface chemistry, the removal of anionic dyes is mainly governed by the

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acid/base character of the carbon surface: higher basic character favouring the efficiency of the material. To our knowledge, in this work we demonstrate for the first time the unprecedented performance of acidic activated carbons, after a liquid phase thermal treatment with sulphuric acid, in the catalytic wet peroxide oxidation of the anionic azo dye Chromotrope 2R (C2R). This dye was selected as model pollutant because of its current use in the textile industry, its chemical structure and finally, because 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 problems associated with this type of pollution.

## 2. Materials and methods

### 2.1. Reactants

Chromotrope 2R ($C_{16}H_{10}N_2Na_2O_8S_2$, Mr 468.39 [4197-07-3], Colour Index Acid Red 29, molecular structure as shown in Scheme 1) was obtained from Fluka. Hydrogen peroxide (30%, w/v), hydrochloric acid (37 wt.%), sodium hydroxide (98 wt.%) and sodium chloride (99.5 wt.%) were obtained from Panreac. Sulphuric acid (96–98 wt.%) was obtained from Riedel-de-Haën. All chemicals were used as received without further purification. Distilled water was used throughout the work.

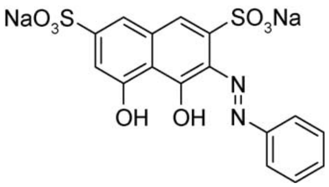
### 2.2. Activated carbons

Four different activated carbon samples were considered in this work: the activated carbon Norit ROX 0.8 (AC), as it is, and chemically modified by liquid phase treatments with hydrogen peroxide (ACHP), sulphuric acid (ACSA) and nitric acid (ACNA). 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% (w/v) 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.

### 2.3. Catalysts characterization

Textural characterization was performed in a Quantachrome NOVA 4200e $N_2$ adsorption analyser. The surface chemistry of the carbon materials was characterized by (i) their point of zero charge (PZC), determined by pH drift tests; (ii) the concentration of acidic and basic sites, using titration techniques and (iii) the nature of the oxygen containing groups on the materials surface, identified by temperature programmed desorption (TPD).

PZC was determined by pH drift tests following the procedure described elsewhere [19]. Five solutions with varying initial pH were prepared using 0.01 M or 0.1 M HCl/NaOH solutions and NaCl (0.01 M) as electrolyte. 50 mL of each solution was contacted with 0.15 g of carbon sample and the suspension left under stirring for 24 h and the equilibrium pH measured. The PZC value of each carbon sample was determined intercepting the obtained final pH versus initial pH curve with the straight line final pH = initial pH.



Scheme 1. Molecular structure of Chromotrope 2R.

The concentration of acidic sites at the materials surface was determined adding 0.2 g of each catalyst sample to 25 mL of a 0.02 M NaOH solution. The resulting suspension was left under stirring for 48 h at room temperature. After filtration to remove the solid material, the residual $HO^-$ was titrated with a 0.02 M HCl solution. The concentration of acid sites at the carbon surface was calculated subtracting the moles of NaOH at the end of stirring from the moles of NaOH initially present in the suspension and dividing this value by the mass of material. The concentration of basic sites was determined in a similar way, this time adding the carbon sample to a 0.02 M HCl solution and titrating the resultant solution after stirring and filtration with a 0.02 M NaOH solution. Phenolphthalein was used as indicator in the titrations.

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 mL $min^{-1}$, STP). The mass signals $m/z$ = 28, 44, 48 and 64 were monitored during the thermal analysis. The amounts of CO and $CO_2$ were calibrated at the end of each analysis with pure CO and $CO_2$ gases, with main mass signals $m/z$ of 28 and 44, respectively. After acquisition, the mass signal $m/z$ = 28 monitored during the thermal analysis for CO was corrected in order to eliminate the influence of $CO_2$ on CO evolution, since one of the fragments in the mass spectra of $CO_2$ occurs at $m/z$ = 28. The mass signal corresponding to the release of SO ($m/z$ = 48) was also monitored, since it is an important fragment in the mass spectra of $SO_2$, with a peak intensity of 49% to that of $SO_2$ [20]. The amounts of $SO_2$ were calibrated with sulphanilamide, which releases $SO_2$ upon thermal degradation. After the treatment of the acquired data, the TPD spectra of CO, $CO_2$ and $SO_2$ (in $\mu$mol $g^{-1}$ $s^{-1}$) were obtained.

### 2.4. Catalytic runs

All the oxidation reactions were performed in a 500 mL well-stirred glass reactor equipped with a condenser, a pH measurement electrode, a temperature measurement thermocouple and a sample collection port. The reactor was heated by immersion on a thermostatic water bath, monitored by a temperature controller. Agitation of the reaction mixture was provided by a magnetic stirrer.

In a typical oxidation run the reactor was loaded with 250 mL of water pollutant solution (C2R with a concentration of 100 mg/L) and for CWPO runs the desired load of catalyst (0.5 g/L). Then, the reactor was heated to the desired reaction temperature (323 K). After stabilization of temperature, the solution pH was adjusted to three using 1.0 or 0.1 M solutions of NaOH or $H_2SO_4$. A calculated volume of hydrogen peroxide (6%, w/v) was injected into the system, before starting the reaction, to give the desired concentration inside the reactor (34.6 mM, corresponding to approximately five 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.

### 2.5. Analytical methods

Small aliquots were withdrawn periodically from the reactor to be further analyzed for azo dye concentration, determined by UV–vis spectrophotometry (Varian Cary 50 Scan). The maximum