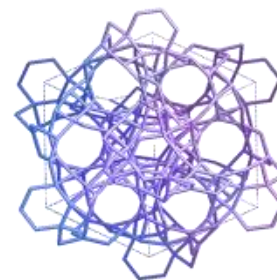




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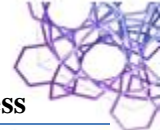
**CATALYSIS:  
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**Instituto Superior Técnico**

Salão Nobre – Pavilhão Central

8<sup>th</sup>-9<sup>th</sup> October 2012



### P39. Carbon nanotubes: a suitable material for catalytic wet peroxide oxidation of organic pollutants?

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#### Introduction

Carbon materials, such as activated carbons (AC), graphite and activated carbon xerogels, have been explored as metal-free catalysts for the catalytic wet peroxide oxidation (CWPO) of bio-refractory organic compounds, such as azo dyes and phenolic compounds [1-3]. At the same time, the application of carbon nanomaterials in catalysis, such as carbon nanotubes (CNT), has grown exponentially [4]. In the present work, commercial multiwalled carbon nanotubes (MWNT) were used in the CWPO of 2-nitrophenol and its activity compared to a commercial AC, used as received and after chemical modifications.

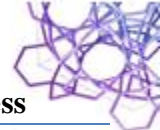
#### Experimental

Batch experiments were performed in a 500 mL well-stirred (500 rpm) glass reactor, loaded with 250 mL of 2-nitrophenol 100 mg L<sup>-1</sup>, considering an adsorption/reaction time of 150 min, being the typical conditions:  $T = 303$  K, pH = 3 and adsorbent/catalyst load = 0.1 g L<sup>-1</sup>. In the CWPO runs, a calculated volume of H<sub>2</sub>O<sub>2</sub> (6 wt. %) was injected into the system after catalyst addition, in order to reach the desired concentration of 34.6 mmol L<sup>-1</sup>.

AC (Norit ROX 0.8) was ground to particle sizes ranging from 0.106 mm to 0.250 mm, being afterwards subjected to several chemical modifications: liquid phase treatment with concentrated sulphuric acid at 423 K (ACS); nitric acid oxidation at boiling temperature (ACN) followed by hydrothermal treatment with urea at 473 K (ACNU); and a gas-phase thermal treatment at 873 K under a N<sub>2</sub> flow (ACNUT). These treatments allowed the production of AC materials with different surface chemistry (pH<sub>PZC</sub> values ranging between 1.6 and 7.6). MWNT were purchased from Sigma-Aldrich (ref. 677248) and used without further treatment. These MWNT are characterized by internal diameters between 2 and 6 nm, external diameters between 10 and 15 nm and lengths between 0.1 and 10 µm, with a composition of iron oxide (III) lower than 5%.

#### Results and discussion

The conversion curves of 2-nitrophenol in CWPO runs performed under the typical conditions referred in the experimental section, testing all the considered materials, are collected in Figure 1a. These experiments show that the removal efficiency depends on the surface chemistry of the used AC, being particularly favored for materials with basic character. On the other hand, it is also observed that the MWNT are able to remove 2-nitrophenol in a substantially larger extent than any of the other materials. A removal higher than 90% after 150 min of reaction is observed, whilst the best AC material is only able to remove about 30% during the same time interval. In face of this astonishing result MWNT were selected for further studies (Figure 1b): first, the extent of adsorption was evaluated performing an adsorption run with MWNT at the same conditions used in CWPO; second, a blank experiment was performed with 2-nitrophenol and H<sub>2</sub>O<sub>2</sub>, to identify a possible non-catalytic effect; finally, since the MWNT contain iron oxides in its composition, the effect of homogeneous catalysis promoted by iron leached during CWPO was simulated, using an Fe<sup>3+</sup> solution as catalyst with the same concentration of iron leached as determined by atomic absorption at the end of the



CWPO experiment (*i.e.*,  $0.024 \text{ mg L}^{-1}$ ). It can be observed that the studied effects are significantly lower than the removal obtained when the MWNT are used as catalysts, suggesting that MWNT are effectively active catalysts for CWPO.

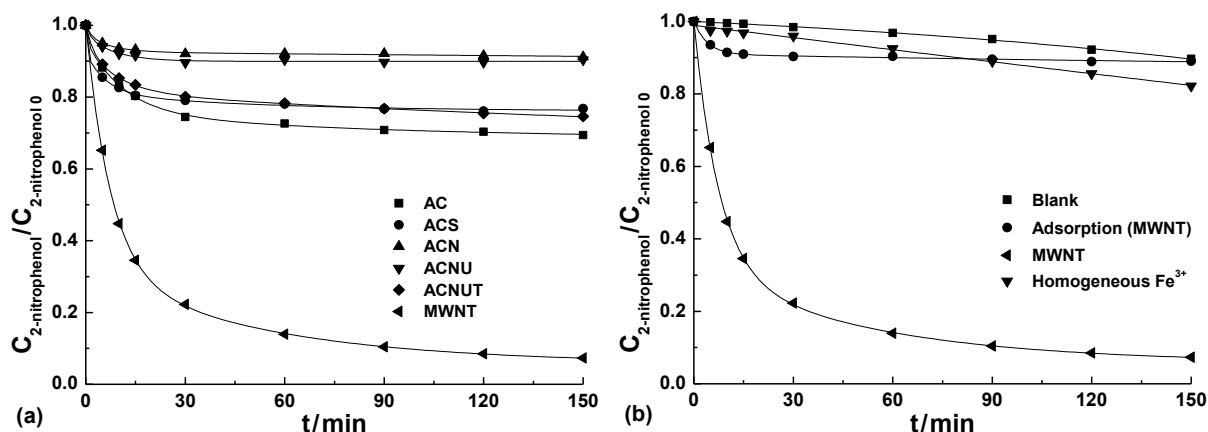


Figure 1. Conversion curves for 2-nitrophenol obtained in CWPO runs performed under typical conditions with all the considered materials (a) and in the study performed with the MWNT (b).

## Conclusions

The results obtained suggest that MWNT are active and suitable catalysts for catalytic wet peroxide oxidation. Further studies are envisaged to fully understand the mechanisms involved in this process.

## Acknowledgements

Work supported by project PTDC/AAC-AMB/110088/2009 and partially by project PEst-C/EQB/LA0020/2011, financed by FEDER through COMPETE - Programa Operacional Factores de Competitividade and by FCT - Fundação para a Ciência e a Tecnologia. AMTS acknowledges financial support from POCI/N010/2006.

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