



Removal of 2-nitrophenol by catalytic wet peroxide oxidation using carbon materials with different morphological and chemical properties



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ABSTRACT

Carbon materials with distinct morphological and chemical characteristics, namely activated carbons, carbon nanotubes, glycerol-based carbon materials and carbon xerogels, were tested for the removal of 2-nitrophenol (2-NP) in aqueous solutions, either by pure adsorption or by catalytic wet peroxide oxidation (CWPO).

The results obtained in adsorption experiments carried out at pH 3, $T = 323$ K, adsorbent load of 0.1 g L^{-1} and 2-NP concentration of 100 mg L^{-1} , show that, in general, the activated carbons have superior adsorption performances compared to the other carbon materials tested, exhibiting removals of 2-NP up to 316 mg g^{-1} after 150 min of adsorption.

In the CWPO experiments, whilst the activated carbons and carbon xerogels were not able to improve the removal of 2-nitrophenol, in comparison with the removals observed in pure adsorption experiments performed at the same conditions, the use of carbon nanotubes (CNT) and a glycerol-based carbon material (GBCM) resulted in increments in the removal of 2-NP as high as 83% and 56%, respectively. Removals of about 80% after only 30 min and higher than 90% after 150 min of reaction (equivalent to 929 mg g^{-1}) are reached when using CNT as catalysts. The leaching of Fe (present as impurity in the CNT) at the end of the CWPO experiment was found to be negligible. The opposite was observed for classical iron supported on activated carbons, with catalytic activities resulting from the homogeneous contribution of Fe that is leached to the liquid phase. The superior performances found for CNT, makes this catalyst a promising system for CWPO.

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1. Introduction

The complexity of industrial wastewaters is increasing nowadays, following the industry's demand towards new products and needs. In particular, nitrophenols are toxic and bio-recalcitrant chemical compounds, inhibitory to some microorganisms [1–5], therefore they can have a negative impact on conventional biological wastewater treatment processes and other treatment options, such as catalytic wet peroxide oxidation (CWPO), should be considered. CWPO, an advanced oxidation process (AOP) involving the use

of hydrogen peroxide (H_2O_2) as oxidation source and a suitable catalyst (typically iron based catalysts) to promote its decomposition through the formation of hydroxyl radicals (HO^\bullet), exhibiting high oxidizing potential and serving as effective species in the destruction of a huge range of pollutants [6,7], is especially attractive due to the use of mild conditions, simple equipment and environmental safety of H_2O_2 [8]. Although the use of metal catalysts like iron, either directly in solution (*i.e.*, homogeneous catalysis, the so-called Fenton's reaction), or immobilized onto a support (*i.e.*, heterogeneous catalysis, CWPO), might be useful for the degradation and mineralization of organic pollutants in water [9,10], it raises difficulties, like the loss of activity of the heterogeneous catalysts due to Fe leaching [11,12] and/or the need for a complicated final chemical-driven separation step for the removal of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions, which are often generated in quantities greater than the limits allowed by European Union Directives for treated water. Thus, the use of metal-free based catalysts in CWPO is of utmost importance.

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It has been previously shown that carbon materials without any supported phases, mainly activated carbons and activated carbon xerogels, can act as catalysts for the CWPO of organic pollutants in aqueous solutions [13–17].

At the same time, the application of carbon nanomaterials, such as carbon nanotubes, has grown, these materials being nowadays intensively explored in catalysis, either as supports for immobilizing active species or also as catalysts on their own [18,19]. Carbon nanotubes possess high surface areas and their surface chemistry can be easily modified [20]. Likewise, the interest in exploring new forms of carbon materials obtained by *in situ* partial carbonization and sulfonation of natural products, or process by-products, has increased, since they present strong acidic characteristics due to the high surface density of sulphonic acid groups [21–23]—which are known to increase the efficiency of the CWPO process [14]. Accordingly, aiming to explore new forms of carbon based materials without any supported phase with potential catalytic activity for CWPO, distinct types of carbon materials were tested in the present work for the removal of 2-nitrophenol (2-NP) from aqueous solutions: commercial activated carbon Norit ROX 0.8 (as received, and chemically modified by liquid phase and thermal treatments); commercial multi-wall carbon nanotubes obtained from Sigma–Aldrich; a glycerol-based carbon material prepared by partial carbonization of glycerol in concentrated sulphuric acid; and a carbon xerogel prepared by polycondensation of resorcinol with formaldehyde. 2-NP was selected as a model compound representative of other non-biodegradable phenols often found in industrial wastewaters, such as those from pharmaceutical, petrochemical, metallurgical, textile, rubber and plastic industries, refineries, fungicides and even from municipal landfill leachate [24–29].

To the best of our knowledge, this work reports for the first time the application of as-produced multi-wall carbon nanotubes, glycerol-based carbon materials prepared by partial carbonization of glycerol and carbon xerogels, without any supported phases, in CWPO of nitrophenolic compounds.

2. Materials and methods

2.1. Reactants

2-NP ($\text{O}_2\text{NC}_6\text{H}_4\text{OH}$, Mr 139.11 [CAS number: 88-75-5], 98 wt.%), iron(III) nitrate nonahydrate (98 wt.%), resorcinol (99 wt.%) and formaldehyde solution (37 wt.% in water, stabilized with 15 wt.% methanol), were purchased from Sigma–Aldrich. H_2O_2 (30%, w/v) and sodium hydroxide (98 wt.%) were obtained from Panreac. Sulphuric acid (96–98 wt.%), nitric acid (65 wt.%) and urea (65 wt.%) were obtained from Riedel–de-Haën. Methanol (HPLC grade), glacial acetic acid (analytical reagent grade) and acetonitrile (HPLC grade) were obtained from Fisher chemical. Glycerol (99 wt.%) was obtained from Alfa Aesar. All chemicals were used as received without further purification. Distilled water was used throughout the work.

2.2. Carbon materials

Four types of carbon materials were initially considered in this work: the commercial activated carbon Norit ROX 0.8 (AC), a commercial sample of multi-wall carbon nanotubes (>90% carbon basis, O.D. \times I.D. \times L: 10–15 nm \times 2–6 nm \times 0.1–10 μm) obtained from Sigma–Aldrich, ref. 677248 (CNT), a glycerol-based carbon material (GBCM) and a carbon xerogel (CX).

AC is a commercial acid washed extruded activated carbon produced by steam activation, which has a high purity with an ash content of only 3 wt.% (0.02 wt.% Fe). CNT are commercial carbon

nanotubes (Arkema Inc., Graphistrength[®] C100), grown in iron particles by catalyzed chemical vapour deposition, with contents of alumina and iron oxide under 7 wt.% and 5 wt.%, respectively, and without detectable free amorphous carbon [30–32]. Further characterization of CNT can be found in the literature [33,34].

GBCM was prepared by partial carbonization of glycerol adapting the procedure described elsewhere [22]: a mixture of glycerol (10 g) and concentrated sulphuric acid (40 g) was gently heated to 453 K and left at that temperature for 20 min to allow *in situ* partial carbonization and sulfonation. During heating, the liquid gradually got darker and at 418 K the mixture started to foam intensely and quickly thickened and gained density resulting in a black solid which was then cooled, washed and filtered in warm water until the neutrality of the rinsing waters was reached. The resulting material was then calcined under a nitrogen flow (100 cm³ min⁻¹) at 393 K, 673 K and 873 K during 60 min at each temperature and then at 1073 K for 240 min, defining a heating ramp of 2 K min⁻¹.

CX was prepared by polycondensation of resorcinol with formaldehyde (with a molar ratio of 1:2), following the procedure described elsewhere [35]: 9.91 g of resorcinol were added to 18.8 mL of deionised water in a glass flask. After complete dissolution, 13.5 mL of formaldehyde solution were also added. In order to achieve the desired initial pH of the precursor solution (6.1), sodium hydroxide solution was added dropwise under continuous stirring and pH monitoring. The gelation step was allowed to proceed at 358 K during 3 days. After this period the gel was dark red and the consistency of the material allowed the sample to be shaped as desired. The gel was then dried in oven during several days from 333 K to 423 K, defining a heating ramp of 20 K day⁻¹. After drying, the gel was pyrolyzed at 1073 K under a nitrogen flow (100 cm³ min⁻¹) in a tubular vertical oven.

Except for the CNT, all the other materials were ground to obtain particle sizes in the range 0.106–0.250 mm.

2.2.1. Modified activated carbons

The powdered original AC was modified by liquid phase, thermal and hydrothermal treatments, resulting in the production of four additional activated carbon samples, following the procedures reported elsewhere [15,36]: a 50 g L⁻¹ mixture containing AC in concentrated sulphuric acid solution (18 mol L⁻¹) was kept for 3 h at 423 K in a 500 mL round-bottom flask heated by an oil bath; the recovered solids were thoroughly washed with distilled water until the neutrality of the rinsing waters was reached, and further dried in an oven for 18 h at 383 K, resulting in the ACS materials. A 50 g L⁻¹ mixture containing AC in nitric acid (5 mol L⁻¹) was kept for 3 h at boiling temperature, and further dried in an oven for 18 h at 383 K, resulting in the ACN materials; a 40 g L⁻¹ mixture containing ACN in urea solution (1 mol L⁻¹) was kept in a 125 mL stainless steel high pressure batch reactor under its own atmosphere at 473 K for 2 h, the recovered solids being thoroughly washed with distilled water until the neutrality of the rinsing waters, and further dried overnight in oven at 383 K, resulting in the ACNU materials; a gas phase thermal treatment was then applied, in which 1 g of ACNU was heated, under a nitrogen flow (100 cm³ min⁻¹), at 393 K, 673 K and 873 K during 60 min at each temperature and then at 1073 K for 240 min, resulting in the ACNUT materials.

2.2.2. Iron supported activated carbons

Classical iron catalysts supported on activated carbons were prepared using AC and ACS as supports, adapting the procedure described elsewhere [12]: a carbon sample was impregnated by incipient wetness with an aqueous solution of iron nitrate nonahydrate in order to obtain 4 wt.% Fe in the catalyst, dried at room temperature for 24 h, followed by overnight drying at 383 K and calcination in air atmosphere for 4 h at two different temperatures,

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