



Effect of activated carbon surface chemistry on the activity of ZVI/AC catalysts for Fenton-like oxidation of phenol



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ABSTRACT

Activated carbons with different amounts of surface oxygenated groups were used as adsorbents or supports for zero-valent iron (ZVI) catalyst and tested in phenol adsorption and catalytic wet peroxide oxidation, respectively. The results revealed that the surface chemistry of the support plays an important role in phenol adsorption and in the catalytic performance of the respective iron-supported catalysts. ZVI is active when the support has only a limited amount of oxygenated groups on the surface. The presence of acidic oxygenated surface groups is not favorable for the catalytic activity of ZVI in phenol oxidation as well as for phenol adsorption. ZVI supported on activated carbon heat-treated at 900 °C yields the best phenol removal, reaching over 85% after 3 h, under the conditions tested: 150 mg L⁻¹ of initial phenol concentration, initial pH set at 3, 30 °C, and the stoichiometric amount of hydrogen peroxide for achieving complete mineralization.

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1. Introduction

Degradation of refractory organic compounds such as phenol and derivatives from industrial wastewater is of interest due to their biotoxic properties [1–3]. Oxidation techniques carried out at low temperature, as the Fenton process, are able to achieve good results [4–6]. Nevertheless, its application to the treatment of waste water has been limited mainly due to the loss of reagent activity and the need of additional separation steps to remove the homogeneous catalyst (iron-containing waste sludge) from the effluent [6,7]. To overcome these disadvantages, several studies have been performed to develop heterogeneous iron containing catalysts from different iron precursors and support materials, which will be able to generate the desired hydroxyl radicals in the presence of hydrogen peroxide [8–12].

Activated carbons have been used for many years as a good adsorbent and support, but also their use as catalysts on their own is growing [13–17]. One of the advantages of activated carbon (AC) is the possibility of tailoring their physical and/or chemical properties

in order to optimize their performance for specific applications [18]. Moreover, the surface chemistry can play an important role on the catalytic activity [19–21].

In the present study, an alternative solution is proposed, which is based on the use of a heterogeneous catalyst consisting in a home-made zero-valent iron (ZVI) supported on surface modified activated carbon (MAC). The use of this zero-valent iron supported on surface modified activated carbon (ZVI/MAC) can easily overcome the inconvenient subsequent catalyst separation. In addition, the oxidation of the metallic iron, generates *in situ* ferrous iron giving rise to an effective Fenton-type reaction, and also a fast recycling of ferric iron into ferrous iron at the metal surface, which leads to have continuous presence of iron metal for the generation of hydroxyl radicals [22–24].

In this work, a commercial activated carbon (Norit ROX 0.8) was modified by chemical and thermal treatments in order to obtain supports with different surface chemistries, while maintaining the original textural properties as far as possible. The wet incipient impregnation was used for preparing iron catalysts supported on the different activated carbon supports. Then, the performance of the modified supports and catalysts on phenol adsorption and wet peroxide oxidation was evaluated in batch reactor and discussed.

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2. Experimental

2.1. Materials

Phenol (99%) and sodium chloride (99%) were purchased from Panreac. Nitric acid, ($\geq 65\%$), hydrochloric acid ($>37\%$), hydrogen peroxide (30%wt), sodium hydroxide ($\geq 97\%$) and iron nitrate nonahydrate ($>98\%$) were purchased from Sigma Aldrich. Activated carbon Norit ROX 0.8 was used as starting material for further treatments. All chemicals were used as received without further purification. Deionized water was used throughout the work.

2.2. Modification of activated carbon supports and catalyst preparation

Prior to use, the Norit ROX 0.8 activated carbon was crushed and the 25–50 mesh fractions (0.3–0.7 mm) was separated and used as starting material (sample AC0). Activated carbons were modified using chemical and thermal treatments, in order to obtain supports with different surface chemistries. Iron was then supported on these modified activated carbons by incipient wetness impregnation.

2.2.1. Oxidation with nitric acid in liquid phase

The starting activated carbon (sample AC0) was oxidized with HNO_3 using a 125 mL Soxhlet extraction apparatus containing 9 g of activated carbon, connected to a boiling flask and to a condenser. A volume of 250 mL of 6 M HNO_3 was introduced into a 500 mL Pyrex round-bottom flask and heated to boiling temperature with a heating mantle. The reflux was stopped after 3 h. The oxidized activated carbon was extensively washed with distilled water to neutral pH and then dried in an oven at 110°C for 24 h (sample AC1) [25].

2.2.2. Thermal treatment in gas-phase

Sample AC1 was the starting material for the preparation of other samples by gas-phase thermal treatments. The starting material had a large amount of oxygen surface groups that were selectively removed in different amounts (and types) by applying different temperatures. Samples AC1.400 $^\circ\text{C}$, AC1.700 $^\circ\text{C}$ and AC1.900 $^\circ\text{C}$ were obtained by heat treatment of AC1 under a flow of N_2 at $100\text{ cm}^3\text{ min}^{-1}$ for 1 h at 400°C , 700°C and 900°C , respectively, followed by treatment under dry air flow at room temperature for 1 h. The final treatment in dry air is intended to stabilize the surface chemistry of the samples [25].

2.2.3. Preparation of catalysts

The active metal was supported on activated carbons by incipient wetness impregnation of an aqueous solution of iron(III) nitrate nonahydrate. The impregnation was always conducted under vacuum and ultrasonic mixing. The precursor solutions with calculated concentration were added drop wise using a peristaltic pump and the slurry was left at room temperature under ultrasonic mixing for 90 min. After impregnation, the samples were dried at 110°C for 24 h, heat-treated under a nitrogen flow at 400°C for 1 h, and finally reduced at 400°C in hydrogen flow for 3 h (sample ZVI/support). The iron load was maintained constant at 3 wt%. The treatment methods for the activated carbon used in this work are summarized in Table 1.

2.3. Characterization of supports and catalysts

The supports were characterized by N_2 adsorption at -196°C , temperature programmed desorption (TPD), and by determination

Table 1

Abbreviations and description of original, modified and iron supported activated carbons.

Abbreviation	Description
AC0	Untreated AC
AC1	HNO_3 -treated AC0
AC1.400 $^\circ\text{C}$	Heat-treated AC1 under N_2 flow at 400°C
AC1.700 $^\circ\text{C}$	Heat-treated AC1 under N_2 flow at 700°C
AC1.900 $^\circ\text{C}$	Heat-treated AC1 under N_2 flow at 900°C
ZVI/ACX.Y	Iron impregnated on ACX.Y

X.Y: represents the modification conducted on the activated carbon.

of the pH at the point of zero charge (pH_{PZC}). The catalysts were also analyzed by temperature programmed reduction (TPR).

2.3.1. Textural characterization

The textural characterization of the supports and catalyst was based on the N_2 adsorption isotherms, determined at -196°C with a Quantachrome NOVA 4200e equipment. Prior to the measurements, the samples were outgassed at 120°C for 5 h under vacuum. The surface area (S_{BET}) of the samples was calculated by the B.E.T. method, and the specific surface area of the mesopores (S_{meso}) and micropore volume (V_{micro}) were calculated by the t -method.

2.3.2. Surface chemistry characterization

The surface chemistry of the activated carbons was characterized by temperature-programmed desorption (TPD) [25]. The TPD spectra of CO and CO_2 were obtained with a fully automated AMI-300 (Altamira instruments). The carbon sample (0.10 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5°C min^{-1} up to 1100°C under a constant flow rate of He at $25\text{ cm}^3\text{ min}^{-1}$. The amounts of CO ($m/z=28$) and CO_2 ($m/z=44$) released from the carbon samples were monitored with a mass spectrometer (Dymaxion, Ametek). CO and CO_2 were calibrated at the end of each analysis.

The pH at the point of zero charge (pH_{PZC}) was determined by mixing 0.05 g of each sample with 20 mL of 0.01 M NaCl solution with pH values adjusted between 2 and 11, by adding 0.1 M HCl or 0.1 M NaOH solutions. The final pH was measured after 48 h of shaking at room temperature. Blank experiments (without addition of carbon) were also performed for each pH and the values measured after 48 h are considered as the initial pH, in order to avoid the variation of pH caused by the effect of CO_2 present in head space. The pH_{PZC} value of each carbon sample was determined by intercepting the obtained final pH vs. initial pH curve with the straight line final pH = initial pH [26].

2.3.3. Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) analysis allows finding the most appropriate reduction temperature of the metal and to evaluate the effect of modified activated carbons on the metal reducibility. TPR profiles were obtained with a fully automated AMI-200 (Altamira Instruments). The sample (0.15 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 5°C min^{-1} up to 600°C under a flow of 5% (v/v) H_2 in Ar at $30\text{ cm}^3\text{ min}^{-1}$. The H_2 consumption was monitored by a thermal conductivity detector (TCD). The temperature range where reduction occurs could be indicated directly from the H_2 consumption peaks.

2.4. Batch adsorption and catalytic tests

Adsorption and CWPO experiments were carried out in a magnetically stirred batch reactor. The reactor was filled with 100 mL of a phenol aqueous solution (150 mg L^{-1}) and heated by immersion in a water bath at controlled temperature (30°C). The solution

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