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Zero-valent iron supported on nitrogen-containing activated carbon for catalytic wet peroxide oxidation of phenol

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ABSTRACT

Zero-valent iron supported catalysts were prepared through modifying an activated carbon (AC) support with different nitrogen containing precursors; (ethylenediamine, urea and melamine) and impregnating it with 3 wt% of iron. The supports were characterized by N_2 adsorption at −196 °C, elemental analysis (EA), the pH at the point of zero charge (pH_{PZC}) and temperature programmed desorption (TPD). The iron catalysts were also characterized by temperature programmed reduction (TPR). Subsequently, the catalysts were tested in the adsorption and wet peroxidation of phenol. The results from the different characterization techniques demonstrate that the nitrogen-containing groups are successfully introduced into the carbon surface via all the precursors used. The tests of the different modified carbons as adsorbents/catalysts indicated that the adsorption capacity and the efficiency in phenol oxidation are governed by the specific surface area and functional groups present. Both surface chemistry and textural properties of carbons are influenced by the nitrogen source and the type of oxygen functionalities preexisting on the surface. The modified carbon-supported iron catalysts revealed significantly enhanced phenol removal efficiency, reaching over 85% conversion after 3 h, and showed interesting catalytic stability.

1. Introduction

The ever increasing demand for water has caused considerable attention to be focused towards recovery and re-use of wastewaters [1]. Besides, due to the increasing complexity and toxicity of organic pollutants in industrial wastewaters and the more increasingly strict environmental regulations, the toxicity nature must be reduced. Phenol is among the most common water pollutants [2,3] because it is present in the effluent of numerous industrial processes such as oil refineries, petrochemical and pharmaceutical industries [4,5]. This draws the attention of policymakers and scientists to take the necessary measures by studying alternative technologies, such as advanced oxidation processes (AOPs).

AOPs are technologies based on the action of hydroxyl and other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds towards by-products and eventually inert end products [6,7]. Among others, hydrogen peroxide, ozone or oxygen/air can be used as oxidizing agents, the processes being called wet peroxide oxidation (WPO), ozonation and wet air oxidation (WAO), respectively [8–10]. Fenton process mainly operates under relatively mild operating conditions using hydrogen peroxide as oxidant and iron as a catalyst [11].

Fenton process achieves good results so far. However, its application is mainly dependent on the narrow operational pH range, the loss of reagent activity and the need for a subsequent separation step to remove the homogeneous catalyst from the effluent, which significantly increases the cost of the operation [12]. Therefore, taking into consideration the aforementioned inconveniences of Fenton system, a strategy is proposed to prepare a heterogeneous catalyst containing both the catalytic metal (iron) and N-functional groups on the surface of activated carbon (AC).

On one hand, it is well known that AC is widely used as a good adsorbent and supporting material due to its excellent properties in mechanical strength and porous structures [13,14]. On the other hand, the catalytic activity of AC is far from well understood. Besides the direct relationship with the physical properties (surface area, pore volume, etc.) of activated carbon [15], the surface chemistry can play an important role [16–18]. According to the recent work of

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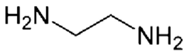
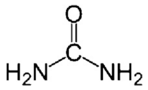
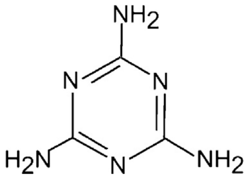
Table 1
Chemical properties of the N-containing compounds used.

N-containing compounds	Molecular formula	Molar mass (g mol^{-1})	Chemical structure	N content (wt%)
Ethylenediamine	$C_2H_8N_2$	60.10		46.59
Urea	CH_4N_2O	60.06		46.62
Melamine	$C_3H_6N_6$	126.12		66.60

Dominguez et al. [19], the effects of physicochemical characteristics of carbon materials on the rate of hydrogen peroxide decomposition were explained using cyclic voltammetry, and the main results indicated that the most important factor in the catalytic activity was the content of metals, in particular iron, this was followed by the specific surface area and finally the content of surface oxygen groups.

In addition, the presence of a chelating agent in homogeneous Fenton has demonstrated to enhance the oxidation capacity [20], either by powering the oxidation potential or keeping the iron in solution at higher pH, although the addition of a new compound in solution is clearly an inconvenience [21]. Although, some interest has been showed in using nitrogen-containing carbon materials as metal catalyst supports [22], to the best of our knowledge, there are no data about their application in the catalytic wet peroxide oxidation (CWPO) process, but there are some recent studies on catalytic wet air oxidation (CWAO). Aminated activated carbon as a catalyst in the CWAO of cooking wastewater has been studied by Chen et al. [23]. The COD removal in CWAO of organic compounds by nitrogen containing AC was higher than that of the untreated AC and suggested that nitrogen-containing functional groups contributed to the enhanced activities of ACs. A similar study was reported by Ayusheev et al. [24], focusing on the effect of nitrogen content in N-doped carbon nanofibers (N-CNFs) on the catalytic activity of Ru/N-CNFs in the wet air oxidation of phenol. Ru-containing catalysts and nitrogen in N-CNFs was found to be responsible for both the increased activity and stability of the catalysts. Moreover, this study illustrates that the increase in catalytic activity is related with several factors: (1) introducing a heteroatom into carbon materials changes the acid-base properties of the support surface; (2) it makes possible to control the size of the supported metal particles; (3) using a support of higher conductivity leads to enhanced chemical reactivity for electron transfer process in a catalytic system.

Therefore, the main objective of this work is to prepare surface modified activated carbon materials (for utilisation as supports/catalysts) using different N-containing groups, i.e. ethylenediamine (EDA), urea or melamine. Prior to introducing the N-functional groups on the AC surface, the activated carbon was oxidized by HNO_3 and/or subsequently activated by thionyl chloride treatment. Later, iron impregnated and then their performances where evaluated on phenol adsorption and wet peroxide oxidation.

2. Experimental

2.1. Materials

Activated carbon Norit ROX 0.8 was used as starting material for further treatments. Phenol (99%) and sodium chloride (99%) were purchased from Panreac. Nitric acid (≥65%), hydrochloric acid (>37%), hydrogen peroxide (30 wt%), urea (98%), sodium hydroxide (≥97%) and iron nitrate nonahydrate (>98%) were purchased from Sigma–Aldrich. Ethylenediamine (>99%) was obtained from Merck. Thionyl chloride (>99%), melamine (≥99%) and toluene (>99%) were purchased from Fluka. The main physico-chemical properties of these N-containing compounds are presented in Table 1. All chemicals were used as received without further purification. Deionised 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 granules of 25–50 mesh size (0.3–0.7 mm) were separated and used as starting material (Sample AC0). Activated carbons were modified using a combination of surface modification protocols described below, in order to obtain supports having N-containing surface groups. 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) [18].

2.2.2. Activation with thionyl chloride

Thionyl chloride was used as a linking agent on the surface of AC for the attachment of N-functional groups [25]. About 12 g of the oxidized activated carbon (AC1) were subsequently activated with 40 mL of 5% solution of thionyl chloride in toluene for 5 h at 70 °C. The carbon was then rinsed at least two times with toluene, and then purified by Soxhlet extraction with toluene for 2 h, and dried in an oven at 110 °C for 24 h (sample AC2) [26–28].

2.2.3. Functionalization with ethylenediamine, urea and melamine

Samples AC1 and AC2 were the starting materials for functionalization with N-containing compounds. The functionalization of activated carbons with EDA, urea or melamine can be conducted directly (using sample AC1) or indirectly (using sample AC2). In the direct method, amine groups of these compounds condense with carboxyl groups on AC to generate surface amide groups. In the