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Highly efficient application of activated carbon as catalyst for wet peroxide oxidation

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ABSTRACT

This paper addresses the improved performance of activated carbons in catalytic wet peroxide oxidation (CWPO) of phenol as target compound. Initial cyclic voltammetry experiments show that hydrogen peroxide and phenol compete for the same active sites on the carbon surface. Then, a significant coverage of the carbon surface by phenol molecules is the approach attempted to increase the efficiency of hydrogen peroxide and the performance of the oxidation process.

In this work, two commercial activated carbons, with different physical and electrochemical properties have been tested. The results demonstrate that working at high phenol concentration (5 g/L) and phenol/carbon mass ratio (2), unprecedented hydrogen peroxide efficiencies of around 100% are achieved, allowing high oxidation and mineralization degrees, *i.e.* 97% phenol and 70% TOC conversions at 80 °C with the stoichiometric dose of hydrogen peroxide required for complete mineralization of phenol. The oxidation route of phenol in the presence of activated carbon is also studied and a reaction pathway proposed. Resorcinol was a new by-product detected whose formation occurs upon reaction on the carbon surface. Condensation by-products, typically formed in Fenton oxidation of phenol, were not found in the effluents but adsorbed on the carbon surface causing a progressive deactivation upon use. The activity can be easily recovered by oxidative thermal regeneration (350 °C, 24 h).

1. Introduction

Catalytic wet peroxide oxidation (CWPO) relies on the oxidation of organic pollutant in water under relatively mild operating conditions (T = 25–100 °C, P = 0.1–0.5 MPa) using hydrogen peroxide as oxidant.

Activated carbons (ACs) have been used as catalysts in CWPO [1–11] since they exhibit donor–acceptor surface properties allowing hydrogen peroxide decomposition into radical species through an electron transfer reaction similar to the Fenton mechanism [12,13]. In this way, AC and AC^+ act as reduced and oxidized catalyst states leading to the formation of $^{\bullet}OH$ and $^{\bullet}OOH$, respectively [4,5,8,10,14,15]. As studied in a previous work [16], the electrochemical capacity of a carbon material dictates the carbon activity in this reaction. Cyclic voltammetry analysis combined with kinetic studies have shown that the apparent first-order rate constant for hydrogen peroxide decomposition is linearly dependent on the exchange current, and that the limiting step in this reaction is the regeneration of the active sites by the reduction of the carbon surface.

In spite of the widely demonstrated ability of activated carbons for hydrogen peroxide decomposition, the removal of organic pollutants in CWPO with bare ACs proceeds mostly through adsorption [1,2,11,13]. Low activities for removal of phenolic compounds [2,8,9,11] and moderate for dyes [3–5,7] have been usually observed even at hydrogen peroxide doses significantly higher than the stoichiometric ones for the complete mineralization of phenol. The efficient consumption of hydrogen peroxide is of main concern in CWPO with activated carbons. AC promotes parasitic reactions consuming $^{\bullet}OH$ and $^{\bullet}OOH$ radicals to produce oxygen, a non-effective specie under the temperature range commonly used in wet peroxide oxidation. That represents a serious drawback for the potential application of AC in CWPO. For this reason, transition metals, in particular Fe, and metal oxides have been incorporated onto the carbon surface. The high surface area of activated carbons provides multiple anchoring sites for the metal and a high capacity for the adsorption of organic molecules. However, metal leaching has been commonly observed.

A different approach to improve the performance of ACs has been attempted through chemical modification of the carbon surface addressed to introduce acid or basic oxygen groups

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[3–5,7,9]. According to some results, acid groups decrease the activity of the virgin AC for hydrogen peroxide decomposition [5–7,9,15,17], while the incorporation of basic groups does the opposite [4,11,15,17]. In both cases, oxidation is enhanced but obviously due to different effects. The acid groups with electron withdrawal capacity substrate electrons from the basal planes of the carbon surface thus restricting their availability to hydrogen peroxide molecules. Therefore, radical species from hydrogen peroxide are formed more gradually and the extension of the parasitic reactions decreases while increasing the breakdown of organic species [9]. On the other hand, basic groups (pyrones, chromenes, ethers and carbonyls) enhance the decomposition of hydrogen peroxide into radicals species.

Herein, we offer a novel approach to enhance the selectivity of AC toward phenol oxidation and mineralization in detriment of the scavenging reactions, with the aim of maximizing the efficiency of hydrogen peroxide consumption. This approach consists of carrying out the CWPO at relatively high phenol concentration (5 g/L), substantially above the most commonly used and also, high phenol/carbon mass ratio. Then, a significant coverage of the carbon surface by the organic molecules should decrease the rate of radical formation from hydrogen peroxide decomposition and makes phenol more easily available to the oxidizing radicals. Both aspects reduce the occurrence of parasitic scavenging reactions on the carbon surface.

Two commercial activated carbons with different physical and electrochemical properties have been tested in CWPO using phenol as target compound. Their activity has been evaluated in relation with hydrogen peroxide decomposition and phenol oxidation and mineralization. Also, the phenol oxidation pathway in the presence of activated carbon has been investigated. Regeneration of the activated carbon after its use has been studied as well.

2. Experimental

2.1. Reagents

Aqueous phenol solutions were prepared with phenol (5 g/L) (Sigma–Aldrich) at pH 3.5 using HCl 1 M (Panreac). Hydrogen peroxide solution (30% w/w) was purchased from Sigma–Aldrich. Working standard solutions of phenol (Sigma–Aldrich), hydroquinone (Sigma–Aldrich), resorcinol (Sigma–Aldrich), catechol (Sigma–Aldrich), *p*-benzoquinone (Sigma–Aldrich), acetic acid (Sigma–Aldrich), formic acid (Sigma–Aldrich), malonic acid (Sigma–Aldrich), maleic acid (Sigma–Aldrich) and oxalic acid (Panreac) were prepared for equipment calibration. Other reagents used in the analysis were H_2SO_4 (Panreac), C_2H_3N (Riedel-deHaën), Na_2CO_3 (Panreac), $NaHCO_3$ (Merck), $Na_2S_2O_8$ (Panreac), HPO_4 (Fisher), $C_6H_4COOHCOOK$ (Aldrich), $TiOSO_4$ (Riedel-deHaën), $C_{16}H_{18}N_3ClN_3S$ (Panreac) and CH_3OH (Sigma–Aldrich). These reagents are of analytical grade and were used without further purification. All the solutions were prepared with milli-Q water.

2.2. Activated carbons

Commercial activated carbons were supplied by Merck (AC-M, ref.: 102514, granular) and Panreac (AC-P, ref.: 121237, $d_p < 100\ \mu m$). Before use they were sieved to yield a particle size ranged from 80 to 100 μm. Also, the samples of activated carbons were pre-washed with a phenol solution by contacting 0.125 g of AC with 50 mL of the 5 g/L phenol solution at 80 °C during 24 h under vigorous stirring. The resulting samples were identified as w-AC-P and w-AC-M.

2.3. Characterization of the activated carbons

Different techniques were used for the characterization of the ACs used as catalysts. X-ray diffraction (XRD) was performed in a Siemens Model D5000 X-ray diffractometer, using Cu Kα (8.04 keV) radiation, and a step of 0.02°/s for $2\theta = 5°–100°$. XRD data were analyzed with PDF 2000 (JCPDS-ICDD) software.

Thermogravimetric analysis (TGA) was carried out in a Mettler-Toledo TGA/SDTA851^e thermobalance. The sample powders were heated in air from 50–900 °C at heating rate of 10 °C/min. The textural properties of fresh and pre-washed carbons were characterized from the 77 K N_2 adsorption/desorption isotherms using a Micromeritics Tristar apparatus, outgassing the samples overnight at 150 °C to a residual pressure of $<10^{-3}$ Torr. The external or non-microporous surface area (A_{ext}) and the micropore volumes (V_m) were calculated by the *t*-method. Elemental analysis was performed in a LECO Model CHNS-932 apparatus. Total reflection X-ray fluorescence (TXRF) (Extra-II Rich & Seifert spectrometer) was used for elements identification and iron content in the carbon ashes. The surface oxygen groups (SOGs) were quantified by temperature-programmed desorption (TPD). The analysis was carried out as follows: a sample of 100 mg of carbon was placed in a quartz tube and heated at 10 °C/min from room temperature up to 900 °C. N_2 was used as carrier gas at 1000 N mL/min. The evolving CO_2 and CO were analyzed in a SIEMENS (mod. Utramat 22) gas analyzer. Deconvolutions of the TPD spectra were adjusted to multiple Gaussian function by Peakfit 4.12 software.

Cyclic voltammetry measurements were carried out at room temperature and ambient pressure in a conventional three-electrode electrochemical cell, using a computerized potentiostat (Autolab PGSTAT 302, Eco Chemie) controlled by GPES software. A glassy carbon rotating disk electrode was used as substrate for the carbon samples, a gold electrode as the counter electrode, a saturated Ag/AgCl, KCl electrode as the reference and HCl solution (pH 3.5) as electrolyte. The carbon electrode was prepared by dispersing 6 mg of the activated carbon (as-received or pre-washed with a phenol solution) in Milli-Q water (730 μL) with ultrasonic agitation (Hyelscher, UP50H) and dropped on the glassy carbon electrode (20 μL) to obtain a uniform catalyst film. The prepared electrodes were subjected to cyclic voltammetry measurements (10 mV/s) under nitrogen atmosphere in the absence (background) and the presence of hydrogen peroxide (25 g/L) within the potential range from −0.6 to 1 V. From these experiments, the coulombic charge (*CC*) and the exchange current (i_o) were calculated. More detailed description of this analysis has been reported elsewhere [16].

2.4. Wet peroxide oxidation experiments

The oxidation tests were carried out batch-wise in a magnetically stirred three-necked glass reactor equipped with a reflux condenser. In a typical experiment, 45 mL of aqueous phenol solution (5 g/L) at pH 3.5 (HCl) were placed in the reactor, along with 0.125 g of activated carbon and the content was heated to 80 °C. Once this temperature was reached, 5 mL of an adjusted concentration of hydrogen peroxide solution were injected and the stirring at 1200 rpm started. Effluents at different reaction times were taken from the reactor and immediately analyzed. After 24 h of reaction, the heating was switched-off and the flask cooled to room temperature in cold water. Then, the catalyst was separated by filtration (0.45 μm Nylon filter) and oven-dried at 60 °C. Additionally, homogenous contribution was assessed by working in the absence of catalyst (blank experiment). Hydrogen peroxide decomposition experiments with activated carbons in the absence of phenol were also carried out. Adsorption runs were performed under the same operating conditions and procedure as the oxidation tests but in the