



Effect of transition metal impregnation on oxidative regeneration of activated carbon by catalytic wet air oxidation



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ABSTRACT

Impregnation of a commercial activated carbon (AC) with transition metals was investigated to extend its reuse as phenol adsorbent after regeneration by catalytic wet air oxidation (CWAO). Iron and copper catalysts were prepared with varied metal dispersions and oxidation states by using different heat treatments. The main feature of the iron catalysts was to reduce the phenol oligomerization due to oxidative coupling, while the copper catalyst was prone to leaching promoting homogeneous reaction. However their regeneration efficiency was not significantly improved with respect to the starting AC due to an increased adverse effect of CWAO itself on their adsorptive properties.

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1. Introduction

Phenols are commonly found in wastewater discharges as major compounds of oil refineries, coal conversion processes, petrochemical and pharmaceutical industries, steel and resin manufacturing plants [1]. Due to their low biodegradability, phenol and derivatives can be toxic even at low concentration and cause undesirable effects on marine wildlife [2] and human health [1].

Therefore phenol is probably the most investigated pollutant in the numerous studies examining physical and chemical wastewater treatments in complement or replacement of the usual biological processes. For instance, adsorption on activated carbon (AC) is a popular technique to remove phenol because of its high efficiency, simplicity of design and operation, and low energy cost [3–5]. However adsorption provides only a temporary solution by displacing the pollution and the spent activated carbon itself may be considered as a hazardous material which requires regeneration or incineration. Several techniques of regeneration have already been studied based either on desorption or pollutant decomposition [6,7]. Thermal regeneration using steam or inert gas stream

(generally operated at temperatures above 700 °C) [8], supercritical wet oxidation [9] and wet air oxidation (WAO) [10,11] are proved to be efficient, but they request high energy consumption and/or expensive equipment. When WAO is operated directly on AC, the later can act as an efficient catalyst, tempering the required conditions of temperature and pressure [12,13].

In this context, a sequential adsorption/oxidation (AD-OX) process has been developed which combines low-cost effective adsorption onto activated carbon (AC) to in-situ regeneration of the adsorbent by catalytic wet air oxidation (CWAO) [14–16], thereby destroying (at least partially) adsorbed organic pollutants. In this process the main wastewater stream is thus treated at ambient conditions, yielding energy saving with respect to the continuous oxidation. Furthermore remaining degradation products should be less an issue (with respect to their possible toxic effects) as they would be more readily extracted from AC during the oxidation step than during the next adsorption. However the whole process performance suffers from a dramatic loss of AC adsorption capacity after the first cycle, mainly due to the deposit of phenolic oligomers formed during oxidation. Several works have suggested that incorporation of inexpensive transition metals onto AC surface could help to preserve its porous structure, besides increasing phenol abatement and mineralization [17–19]. For instance, Quintanilla et al. [18] observed a 89% decrease in the BET surface area of a commercial activated carbon after use for the continuous oxidation of

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phenol, but a decrease of only 40% for the same carbon impregnated with 2.5 wt% of Fe. Sheintuch et al. [6] also compared the regeneration efficiency of virgin and 5–10 wt% metal oxide loaded activated carbons after saturation with phenol. The catalyst was prepared by wet impregnation of AC with a mixture of copper, iron and chromium salts and regeneration was done by flowing air or 5% oxygen in nitrogen at 240–290 °C. The authors concluded that the presence of metals was required to fully restore the adsorption capacities of AC which then could be reused over 10 cycles.

The aim of this work is to investigate the effect of iron or copper oxide deposit on AC activity in CWAO and to extend its lifetime as an adsorbent by improving its regeneration under mild oxidative treatment. For that purpose, transition metal impregnated ACs were tested in repeated adsorption/oxidation cycles performed in a fixed bed set-up, as well as in “standard” batch oxidations in an autoclave reactor.

2. Materials and methods

2.1. Activated carbon and metal sources

A granular activated carbon (AC) produced from wood (Merck 2514) was used as a reference, as it had proved its activity in the CWAO of phenol [12,20] and AD-OX process [15]. It was received in the form of millimeter-sized pellets and sieved to get the 1.2–1.6 mm fraction. Its textural properties are reported in Table 1, showing both meso- and micro-porosity and a high surface area (960 m²/g).

This AC was impregnated using iron or copper nitrate as this precursor was found to yield well anchored and well dispersed catalysts [21,22]. Owing to the high water solubility of these salts (more than 1 kg of hydrated salt/kg of water at 20 °C [23]), concentrated precursor solutions were used, containing 598 and 314 g/L of Fe(NO₃)₃·9H₂O and Cu(NO₃)₂·3H₂O, respectively.

2.2. Metal deposition on activated carbon

5 wt% metal loaded activated carbons were prepared using incipient-wetness impregnation at ambient temperature. The preparation consisted in contacting during one hour the activated carbon with a small volume of precursor solution, equivalent to 110% of the AC porous volume [24]. 15 g of catalyst were prepared at once.

Impregnation was followed by overnight drying at 110 °C. Two protocols were tested for subsequent calcination carried out in a muffle furnace. The first one (a) consisted in heating the solid up to 200 °C under air (with two successive ramps of 0.67 °C/min and 1.67 °C/min) and maintaining this temperature for 4 h (corresponding solids were labeled Fe/ACa and Cu/ACa), while the second one (b) used a calcination temperature of 350 °C (1.4 °C/min ramp and 4 h plateau) under nitrogen flow (Fe/ACb and Cu/ACb).

The first procedure was adopted by Quintanilla et al. [18] for the preparation of their iron on AC catalyst, while the second was used to ensure a complete decomposition of the precursors. According to previous studies [25,26], Fe(NO₃)₃·9H₂O should be entirely decomposed at 160 °C (first into oxyhydroxide), while a temperature of 250 °C might be required to yield CuO from Cu(NO₃)₂·3H₂O. As a significant combustion of the metal impregnated AC occurred when heated up to 350 °C under air (85% weight loss after 4 h), calcination “b” was performed under nitrogen instead.

A reduced iron catalyst (Fe/ACb-H₂) was prepared from Fe/ACb by a subsequent heat treatment under hydrogen flow (ramp of 5 °C/min up to 400 °C, followed by 1 h at this temperature). After reduction, the catalyst was cooled down to room temperature, hydrogen was replaced by argon stream in which oxygen con-

centration was gradually increased from 0.5% to 20% to prevent undesired overheating.

2.3. Characterization of the metal loaded activated carbons

All the synthesized materials were examined by various techniques to analyze the effect of the metal addition on the carbon surface properties and to determine the deposit features according to the preparation method.

2.3.1. Textural properties

The specific area and porosity were measured by nitrogen adsorption/desorption at 77 K using a Micromeritics ASAP 2010 surface area analyzer. Prior to the measurement, the solid sample was evacuated at 200 °C for 2 h.

The specific surface area was calculated from BET plot for relative pressures between 0.01 and 0.2 [27], whereas the mesoporous and microporous volumes were estimated according to Barrett-Joyner-Halenda [28] and Horvath-Kawazoe methods [29] respectively.

2.3.2. Chemical surface properties

Acido-basic properties were measured by the Boehm method [30]: 1 g of solid was placed in 20 mL of aqueous solution containing either NaOH 0.1 N (to neutralize all acid surface groups), NaHCO₃ 0.1 N (for carboxylic ones) or HCl 0.1 N (for basic ones). The suspensions were let three days at room temperature under gentle stirring, then filtrated and each solution was back titrated.

Since surface oxygen groups decompose upon heating at different temperature ranges, thermograms were also recorded on a SDT Q600 thermobalance (TA Instruments) operated under nitrogen flow. A heating rate of 10 °C/min was applied up to 700 °C. The weight loss in the 150–400 °C and 400–700 °C ranges were examined, which should correspond to the decomposition of carboxylic (150–400 °C), then lactone (350–600 °C), phenol and anhydride functions (600–700 °C) [31,32].

2.3.3. Metal deposit characterization

The iron or copper content was checked by ICP/AES analysis (Ultima 2, Horiba Jobin-Yvon) after combustion and acid attack at 150 °C. Three different samples of 0.5 g each were used to get an average value.

The distribution and dispersion of the metal nanoparticles were examined by microscopy coupled to energy-dispersive X-ray spectroscopy for elemental identification. Surface and cut sections of the millimetric pellets were observed on a Hitachi TM 3000 scanning electron microscope and ultramicrotome slices on a JEOL JSM-2100F transmission electron microscope. These observations were complemented by XRD analysis on a Bruker AXS D4 Endeavor to identify the nature of the deposited phases and obtain the mean crystallite size from Scherrer formula.

Based on these characterizations, some catalysts were selected and tested in the AD-OX process.

2.4. Experimental set-ups and procedures

2.4.1. AD-OX process

The successive AD-OX cycles were performed using a small jacketed fixed bed reactor (18 cm high and 1 cm internal diameter) containing about 7 g of solid. The set-up included a continuous liquid feed for the adsorption step, as well as a continuous gas feed, a liquid recycling loop with a pressurized tank, a pre-heating system and a gas-liquid separator for the oxidation step. A set of three-way valves controlled the switch from one mode to another. A schematic diagram was given in Julcour Lebigue et al. [33].

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