



Influence of the iron precursor in the preparation of heterogeneous Fe/activated carbon Fenton-like catalysts

Filipa M. Duarte^a, Francisco J. Maldonado-Hódar^b, Luis M. Madeira^{a,*}

^a LEPAE, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, s/n, 4200-465 Porto, Portugal

^b Department of Inorganic Chemistry, Faculty of Sciences, University of Granada, 18071 Granada, Spain

ARTICLE INFO

Article history:

Received 1 February 2013

Received in revised form 22 March 2013

Accepted 23 March 2013

Available online 29 March 2013

Keywords:

Orange II

Heterogeneous Fenton

Activated carbon

Iron precursor

Catalyst

ABSTRACT

In this work, the influence of the iron salt precursor for the impregnation of a commercial activated carbon (AC) is evaluated in order to choose the best catalyst in the removal of the azo-dye Orange II from water by the heterogeneous Fenton-like process. Three iron salts were used: iron acetate, iron sulphate and iron nitrate, all catalysts being obtained with a content of 7% wt. of iron (Fe/AC) after pre-treatment at 300 °C. The characterization of fresh and used materials was done by different techniques (N₂ and CO₂ adsorption, X-ray diffraction, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy and thermal programmed desorption). The three catalysts presented different textural properties and distinct iron dispersions, along with different locations in the pore structure, thus leading to quite different materials for the envisaged application because those properties strongly influence the different processes that contribute to the dye removal: adsorption, homogeneous Fenton process (due to leached iron) and heterogeneous Fenton-like process (on the catalysts' surface). Iron in solution (or located more externally on the carbon surface) favours the discoloration but can somehow prevent the TOC removal (which also occurs by adsorption). The catalytic behaviour of the samples was correlated with the transformations on their textural and chemical characteristics. Ferrous acetate seems to be the best option for the precursor to use on the basis of activity and particularly stability (i.e., possibility of catalyst reutilization due to low leaching).

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Activated carbons (ACs) are versatile materials with application in several areas, particularly in the environmental protection field. These materials are often used as catalyst supports or act as catalysts on their own [1], and frequently for environmental applications, either in gas- or liquid-phase, the last concerning mainly wastewater treatment. Actually, with the increase of the water pollution caused by industries, concerns regarding the treatment and reuse of wastewater have been growing, from what depends the quality of the human life. The textile sector is one of the production industries that contribute more significantly for this problematic, with millions of tonnes of chemical reagents being launched into textile effluents that must be properly treated before discharge. Advanced oxidation processes arose to destroy those pollutants in an efficient way, being able to oxidize many complex organic pollutants, including dyes (e.g. [2]), unlike most conventional processes [3,4]. The Fenton's reagent is one of the most promising

advanced oxidation processes, and exploits the reaction between iron (II) and hydrogen peroxide for the generation of hydroxyl radicals, highly reactive and unselective species used to destroy the organic matter [5–7]. The homogeneous Fenton process is known for its simplicity, efficiency and low investment cost [8], but it has the important disadvantage of generating iron-containing sludges. To overcome this phenomenon, the metal phase can be supported on a solid porous matrix – the so-called heterogeneous Fenton process.

In heterogeneous advanced catalytic oxidation, ACs can be very useful because they are able to support the metallic catalyst particles in an active and stable way, having also high porosity, high surface area and relatively low cost. Performance of ACs as supports depends on their textural characteristics, surface chemistry, ability to disperse and fix the active phase, and also on the accessibility of the reagents towards the active sites. All these aspects, as well as the behaviour of the AC-based catalyst, depend on the metal to be dispersed. Different transition metals have already been used as the active phase in heterogeneous Fenton's oxidation employing ACs [9,10], but iron is the most common, being also cheap and very active. The iron species can be introduced on the support by impregnation with an iron precursor salt. However, the nature of the iron

* Corresponding author. Tel.: +351 22 508 1519.

E-mail address: mmadeira@fe.up.pt (L.M. Madeira).

precursor might have a crucial role in the final catalyst obtained, as long as it affects the above-mentioned catalyst properties.

In this work, a previously selected commercial activated carbon – Norit RX 3 Extra [11] – was impregnated with three different iron precursors: iron acetate, iron sulphate and iron nitrate (the resulting catalysts were herein called N-Ac₂Fe, N-FeSO₄ and N-Fe(NO₃)₃, respectively, with N referring to the Norit support), in order to choose the best catalyst for the removal of the azo dye Orange II (OII) from an aqueous solution by the heterogeneous Fenton-like process. The influence of the iron salt precursor was evaluated in terms of colour removal, mineralization and leaching (loss of Fe from the catalyst support to the solution); the fresh and used Fe-catalysts were extensively characterized by several techniques with the purpose of relating their performances with their chemical and physical properties.

2. Material and methods

2.1. Reagents

The azo-dye Orange II, also called Acid Orange 7, from Fluka p.a., was used as the model compound to be eliminated. The iron salts used for the impregnation of the activated carbon (AC) were iron acetate (Fe(C₂H₃O₂)₂) with 95% of purity from Aldrich, iron sulphate heptahydrate (FeSO₄·7H₂O) with 98% of purity from Pan-reac, and iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O) with 97% of purity from Riedel-de Haen. Hydrogen peroxide 30% (v/v) was from Normapur. Sulphuric acid 95.0–98.0% from Sigma–Aldrich was used to acidify the OII solutions and sodium sulphite p.a. from Riedel-de Haën was used to stop the homogeneous reactions in the samples taken along reaction time (see Section 2.3).

2.2. Catalysts preparation and characterization

Norit RX 3 Extra (ash content of ca. 2 wt.% according to the supplier's data), commercialized as extruded pellets of approximately 3 × 5 mm, was milled and sieved to get particles in the powder form (<0.15 mm). Three identical fractions of AC powder were separated and each one was impregnated with a different iron salt aqueous solution to obtain a 7% wt. Fe/AC catalyst (the same iron dose used in previous works [9,12]). The iron solutions were prepared by dissolving the required amount of each salt precursor in the minimum volume of distilled water (according to the salt solubility), at room temperature and using magnetic stirring. The impregnation was carried out by adding the precursor solution dropwise and uniformly to the carbon, avoiding the excess of solution. The process was concluded after a homogeneous wetting of the particles [12]. Finally, after drying for 24 h in an oven at 100 °C, the impregnated samples were treated in a He inert atmosphere at 300 °C (heating rate of 10 °C min⁻¹) for 2 h, for the iron salt decomposition. In previous works it was shown that after this thermal treatment both iron acetate and iron sulphate were decomposed – [11] and [13], respectively. Decomposition temperature of iron (III) nitrate is known to be the lowest among the three iron salts, so the thermal treatment applied was also effective in this case.

The textural characterization of the materials was done by N₂ (at 77 K) and CO₂ (at 273 K) adsorption in a Quantachrome Autosorb-1 apparatus. Samples were previously degasified overnight at 120 °C and 10⁻⁶ Torr. This technique provides the analysis of the mesoporous range. CO₂ adsorption allowed obtaining information about the narrower micropores [14]. Both isotherms (N₂ and CO₂) were evaluated by applying the Dubinin–Raduskevich [15] and the Stoeckli [16] equations for determining the micropore volume, W₀, the mean micropore size, L₀, and the microporous surface, S_{mic}. The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) was also

obtained from the N₂ adsorption isotherms. Further details can be found elsewhere [9,17].

Metal dispersion on the carbons' surface was analyzed by X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM), using a Bruker D8 Advance diffractometer and a Philips CM-20 electron microscope, respectively. For X-ray diffraction a Cu Kα X-ray source was used (Cu Kα = 1.5406 Å), with a stepsize of 0.02° and steptime of 2 s, i.e., scan rate of 1°/100 s. XRD was also used for the chemical study of the catalysts' surface – identification of the iron particles nature –, being complemented with X-ray photoelectron spectroscopy (XPS) technique, which allowed obtaining information about the composition of the catalysts' surface, as well as of the iron oxidation state. This technique was carried out using an achromatic Al (Kα) X-ray source in an ESCALAB 200A, VG Scientific system, with the Vision and CasaXPS software for data acquisition and analysis, respectively. Temperature programmed desorption (TPD) experiments were carried out to obtain information about the chemical characteristics of the materials, by heating the samples to 1000 °C in He flow (60 cm³ min⁻¹ – atmospheric conditions of temperature and pressure), with a heating rate of 50 °C min⁻¹. The amount of evolved gases was recorded as a function of temperature using a quadrupole mass spectrometer (Balzers, model Thermocube). The oxygen content was calculated from the amounts of CO and CO₂ released during the TPD experiments.

2.3. Adsorption and catalytic activity

All experiments were carried out in a slurry batch reactor using 1 L of a 0.1 mM OII aqueous solution, with 0.1 g L⁻¹ of solid and 6 mM of H₂O₂ (in the case of catalysis), at 30 °C and pH 3; these conditions were selected upon previous works, e.g. [11–13], being of reference in this area, particularly pH of 3 which is often the optimum one in Fenton-like processes [7,12,18]. Theoretically, 42 mol of H₂O₂ are needed to completely degrade 1 mol of the dye (C₁₆H₁₁N₂NaO₄S + 42H₂O₂ → 16CO₂ + 46H₂O + 2HNO₃ + NaHSO₄). Therefore, the dose employed corresponds to a value above the stoichiometric amount required for complete mineralization (which should yield a ratio of 1); the ratio herein employed was 1.43.

The initial pH of 3 was set by using a 1 M sulphuric acid solution; the jacketed reactor was provided with a thermostatic bath (from Huber) to keep the temperature constant (±0.1 °C), and also with magnetic stirring. After stabilization of the operating conditions, the solid was added, being this the time zero of the adsorption experiments. In the case of heterogeneous Fenton reactions, the time zero corresponded to the time when the impregnated AC was added, together with hydrogen peroxide. OII concentration was continuously measured in terms of absorbance using a Philips PU8625 UV/VIS spectrophotometer at 486 nm (characteristic wavelength of the Orange II molecule, a value at which there is no interference of the oxidation products). Absorbance, temperature and pH data were monitored and saved along time by a home-designed Labview 9.0 interface. Absorbance was then converted into concentration by using an appropriate calibration curve. For evaluating the degree of mineralization (i.e., elimination of total organic carbon – TOC), as well as for the quantification of the loss of iron from the catalyst to the solution (leaching), samples of 10 ml were regularly taken and filtered through Reeve Angel microfibre glass filter paper (pores' diameter of 0.8 μm). The homogeneous reaction in the flask samples was stopped by adding sodium sulphite in excess, once this reagent consumes instantaneously the residual hydrogen peroxide [12,19], and the samples kept in a fridge. TOC analyses were done in a TOC-500A apparatus while leaching was quantified by atomic absorption in an UNICAM 939/959 spectrophotometer.

Download English Version:

<https://daneshyari.com/en/article/40439>

Download Persian Version:

<https://daneshyari.com/article/40439>

[Daneshyari.com](https://daneshyari.com)