



# A ferromagnetic $\gamma$ -alumina-supported iron catalyst for CWPO. Application to chlorophenols



Macarena Munoz<sup>a,\*</sup>, Zahara M. de Pedro<sup>a</sup>, Nieves Menendez<sup>b</sup>, Jose A. Casas<sup>a</sup>, Juan J. Rodriguez<sup>a</sup>

<sup>a</sup> Sección Departamental Ingeniería Química, Universidad Autónoma de Madrid, Crta. Colmenar km 15, 28049 Madrid, Spain

<sup>b</sup> Departamento de Química-Física Aplicada, Universidad Autónoma de Madrid, Crta. Colmenar km 15, 28049 Madrid, Spain

## ARTICLE INFO

### Article history:

Received 10 December 2012  
Received in revised form 25 January 2013  
Accepted 1 February 2013  
Available online 10 February 2013

### Keywords:

Heterogeneous Fenton  
Ferromagnetic catalyst  
Chlorophenol

## ABSTRACT

A ferromagnetic  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported iron catalyst has been prepared and its activity and stability in catalytic wet peroxide oxidation (CWPO) have been compared with those of a previous iron-based conventional catalyst using the same support. Both catalysts were characterized by nitrogen adsorption–desorption isotherms, ICP, TXRF, XRD, XPS, elemental analysis and Mössbauer spectroscopy. The behavior of these catalysts in CWPO of chlorophenols has been related with the nature of the dominant iron species (magnetite or hematite). The results showed that the magnetic catalyst improved significantly the decomposition of H<sub>2</sub>O<sub>2</sub> leading to an increased degradation and mineralization of chlorophenols. Complete conversion of those target pollutants and more than 75% TOC reduction were achieved after 4 h under stoichiometric H<sub>2</sub>O<sub>2</sub> dose, 100 mg L<sup>-1</sup> initial chlorophenol concentration, 1 g L<sup>-1</sup> catalyst, pH 3 and 50 °C temperature. Moreover, complete dechlorination of all the chlorophenols tested was achieved, being the residual organic by-products short-chain acids without significance in terms of ecotoxicity. The catalyst showed a remarkable stability in long-term continuous experiments with limited Fe leaching, below 5% of the initial loading after 100 h on stream. An additional clear advantage of the new catalyst is its easy separation and recovery from the reaction medium by applying an external magnetic field.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Chlorophenols (CPs) are pollutants commonly found in a wide variety of industrial wastewaters since they are used in the manufacture of a diversity of chemical products, like pesticides, herbicides, germicides, fungicides and wood preservatives. These waste streams pose important pollution problems associated to the high toxicity of chlorophenols, which have been listed as priority pollutants by the European Decision 2455/2001/EC [1]. The development of efficient technologies for those industrial wastewaters has focused considerable research efforts in the last years. Advanced oxidation processes (AOPs) have been claimed as potential solution in that respect [2] and in particular the Fenton process has gained a major attention due to its simplicity of design, implementation and operation (near ambient conditions) and its ability to deal with a wide diversity of pollutants [3–5]. Nevertheless, an important drawback of the conventional Fenton is that the catalyst, iron in solution, cannot be retained in the process, requiring further separation to prevent additional water pollution. In this sense, the

use of solid catalysts by immobilization of the active iron over a convenient support offers a practical solution. Research within the last decade has proved that hydrogen peroxide can oxidize organic pollutants in the presence of Fe-bearing solid catalysts in the so-called catalytic wet peroxide oxidation (CWPO). Important efforts have been focused on finding catalysts with adequate activity and stability, taking into account the acidic conditions at which the reaction takes place. So far, mesostructured materials [6–8], zeolites [9,10], pillared clays [11–14] and activated carbon [15,16] have been used as supports to prepare these catalysts. Unfortunately, most of them showed relatively low activities or strong iron leaching due to the acidic pH or the low chemical stability of the supports [16,17]. Recently, iron supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) has proved to be an excellent highly-stable catalyst for CWPO not only with aqueous phenol but with real wastewaters from the cosmetic industry [18,19].

Usually, CWPO catalysts have been used in powdered form ( $d_p < 100 \mu\text{m}$ ), making difficult its separation and recovery from solution. In this sense, ferromagnetic catalysts are receiving increasing attention since they can be easily separated from the liquid phase by applying a magnetic field. Recent studies have been focused on magnetite as catalyst for heterogeneous Fenton oxidation [20,21]. Nonetheless, so far only few papers have been issued

\* Corresponding author. Tel.: +34 91 497 3991; fax: +34 91 497 3516.  
E-mail address: [macarena.munoz@uam.es](mailto:macarena.munoz@uam.es) (M. Munoz).

on the synthesis of mesoporous materials containing ferromagnetic nanoparticles [21–24]. To incorporate magnetic nanoparticles in mesoporous materials, post-synthetic impregnation methods have been generally employed, which require multiple and complicated steps. The post-synthetic incorporation of magnetic nanoparticles in porous hosts could also block the main pores of mesoporous materials [25]. In this sense, a short and simple synthetic procedure should be developed looking for practical application of magnetic catalysts.

In this work, a ferromagnetic and a conventional non-magnetic iron-on- $\gamma$ -alumina catalyst have been prepared and tested in the CWPO of chlorophenols in aqueous solution at atmospheric pressure and at 50 °C. The activity and stability of the catalysts have been analyzed in relation with the dominant iron species. The effect of the chlorine content of chlorophenols was also studied by using 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) as target compounds. The results obtained have been analyzed in terms of hydrogen peroxide decomposition, chlorophenol conversion, overall dechlorination and TOC reduction. The stability of the catalyst was assessed by long-term continuous experiments.

## 2. Materials and methods

### 2.1. Catalysts preparation and characterization

The catalysts were prepared by incipient wetness impregnation of powdered  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $d_p < 100 \mu\text{m}$ ) supplied by Merck (Germany) with a Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O aqueous solution. The Fe load was adjusted to a nominal 4% (w/w). After impregnation, the solids were left for 2 h at room temperature, dried for 12 h at 60 °C and calcined for 4 h at 300 °C. An additional reduction stage in H<sub>2</sub> atmosphere was carried out for 2 h at 350 °C in order to develop magnetic properties in one of the catalysts. Thus, the identification of the catalysts was Fe<sub>2</sub>O<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the non-magnetic and the magnetic catalyst, respectively.

The porous structure of the fresh and used catalysts was characterized from nitrogen adsorption–desorption isotherms at –196 °C using a Micromeritics Tristar 3020 apparatus. The samples were previously outgassed overnight at 150 °C to a residual pressure of 10<sup>–3</sup> Torr. Total iron content was analyzed by inductively coupled plasma (ICP/MS) with a ICP-MS Elan 6000 PerkinElmer Scienc. Elemental analyses of the fresh and used catalysts were carried out in a LECO CHNS-932 Elemental Analyzer. The chlorine content of the used catalysts was determined by total reflection X-ray fluorescence (TXRF), using a TXRF spectrometer 8030c. The iron particles of the Fe<sub>x</sub>O<sub>y</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were characterized by transmission electron microscopy (TEM) at 400 kV (JEOL, mod. JEM-4000 EX). Software “ImageJ 1.44i” was used for counting and measuring particles on digital TEM images (more than 200 nanoparticles were measured per image). The crystalline phases in the catalysts were analyzed by X-ray diffraction (XRD) using a Siemens model D-5000 diffractometer with Cu K $\alpha$  radiation. The iron species in the fresh and used catalysts were also identified by Mössbauer spectroscopy. Mössbauer spectra at room temperature and 77 K were recorded in triangle mode using a conventional spectrometer with <sup>57</sup>Co(Rh) source. The spectra were analyzed by a non-linear fit using the NORMOS program [26] and the energy calibration was made using a  $\alpha$ -Fe (6  $\mu\text{m}$ ) foil. X-ray photoelectron spectroscopy (XPS) was employed for surface iron analysis using a Physical Electronics, model ESCA 5701 apparatus equipped with a Mg-K $\alpha$  X-ray excitation source, 1253.6 eV. Software “Multipak v8.2b” was used for spectrograms deconvolution in order to determine both Fe (II) and Fe (III) species on

the surface of the catalysts. Magnetic measurements were performed using a Quantum Design MPMS XL-5 superconducting quantum interference device (SQUID). The magnetic moment  $M$  was measured as function of applied magnetic field  $H$  at room temperature.

### 2.2. CWPO experiments

CWPO runs were carried out at atmospheric pressure and at 50 °C. All of the experiments in this work were performed in a glass batch reactor (450 mL) equipped with a PTFE stirrer (700 rpm) and a temperature control. The aforementioned temperature has been reported as the optimum for this process [19,27,28], because of the enhanced efficiency of H<sub>2</sub>O<sub>2</sub> consumption. Increasing the temperature above the ambient has demonstrated a beneficial effect on that respect which is crucial in the economy of the process [29]. The initial pH of the reaction medium was adjusted with nitric acid to the optimum value (pH 3) in all the experiments [18]. A starting chlorophenol concentration of 100 mg L<sup>–1</sup> was always used which can be considered a representative concentration of chlorophenols in industrial wastewaters [30–32]. According to previous works [19,33,34], the theoretical stoichiometric amount of H<sub>2</sub>O<sub>2</sub> for complete oxidation of each chlorophenol to CO<sub>2</sub>, H<sub>2</sub>O and HCl, and 1 g L<sup>–1</sup> of powdered Fe<sub>x</sub>O<sub>y</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst ( $d_p < 100 \mu\text{m}$ ) were used in all the experiments.

Long-term experiments were carried out in a 500 mL glass continuous stirred (700 rpm) tank reactor at 2 mL min<sup>–1</sup> flow rate over 100 h using 500 mg of catalyst, 50 °C and initial pH 3. In order to avoid the loss of catalyst from the reactor a Swagelok filter was placed at the exit. The starting 2,4,6-TCP and H<sub>2</sub>O<sub>2</sub> concentrations were 100 and 190 mg L<sup>–1</sup>, respectively.

In each run, samples were periodically withdrawn in order to follow the progress of the reaction. Chlorophenols and the main aromatic by-products were quantified by means of high-performance liquid chromatography (HPLC; Varian Pro-Start 325) using a UV detector and a Microsorb C18 5  $\mu\text{m}$  column (MV 100, 15 cm length, 4.6 mm diameter) as the stationary phase. The analyses were carried out at 270 nm using a 70/30, 55/45 and 45/55% (v/v) mixture of acetonitrile/acetic acid aqueous solution (75 mM) as the mobile phase for 4-CP, 2,4-DCP and 2,4,6-TCP, respectively. Short-chain acids and chloride ion were analyzed by ion chromatography with chemical suppression (Metrohm 790 IC) using a conductivity detector. A Metrosep A supp 5–250 column (25 cm length, 4 mm internal diameter) was used as stationary phase and a 3.2 mM Na<sub>2</sub>CO<sub>3</sub> aqueous solution as the mobile phase. Total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, mod. TOC, VSCH) and the H<sub>2</sub>O<sub>2</sub> concentration was determined by colorimetric titration using the titanium sulfate method [35] with an UV 1603 Shimadzu UV/Vis spectrophotometer. Fe leached from the catalyst to the reaction medium was measured according to the o-phenantroline method [36].

To evaluate the ecotoxicity of the reaction effluents, a standard method (Microtox M500 Analyzer) was used. The Microtox test (ISO 11348-3, 1998) is based on measuring the intensity of the bioluminescence emitted by the marine bacteria *Vibrio fischeri*. The bioluminescence was measured in a M500 Microtox Analyzer (Azur Environmental). The test was carried out at 15 °C, adjusting the osmotic pressure close to 2% NaCl and pH between 6 and 8. The EC<sub>50</sub> is defined as the effective nominal concentration (mg L<sup>–1</sup>) of the target compound that reduces the intensity of light emission by 50% after 15 min contact time. For complex samples, IC<sub>50</sub> is used, defined as the dilution ratio (%) of the sample that yields this 50% light emission reduction. The IC<sub>50</sub> values are inversely proportional to the biological toxicity expressed as toxicity units (TU).

Download English Version:

<https://daneshyari.com/en/article/46329>

Download Persian Version:

<https://daneshyari.com/article/46329>

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