



Improved wet peroxide oxidation strategies for the treatment of chlorophenols



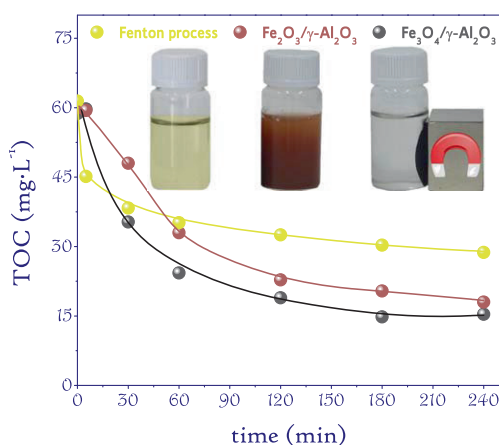
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HIGHLIGHTS

- CWPO of chlorophenols with $\text{Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ catalysts is more efficient than Fenton oxidation.
- Increasing the temperature improves both the oxidation rate and mineralization degree.
- The $\text{Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ catalysts are highly active and stable upon CWPO of chlorophenols.
- CWPO ($\text{Fe}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$) at high temperature is the preferable strategy for chlorophenols oxidation.
- $\text{Fe}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst can be easily recovered from the liquid phase by a magnet.

GRAPHICAL ABSTRACT



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ABSTRACT

Different advanced oxidation strategies have been investigated for the treatment of chlorophenols in aqueous phase with the aim of improving the removal efficiency in terms of mineralization, remanent by-products and kinetics. Those strategies were homogeneous Fenton-like oxidation and CWPO with two different own-prepared $\text{Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ catalysts. The intensification of the process by increasing the temperature has been also evaluated. CWPO of chlorophenols with those catalysts has proved to be more efficient than homogeneous Fenton-like oxidation due to a lower rate of H_2O_2 decomposition allowing a higher availability of hydroxyl radicals along the course of reaction. Increasing the temperature clearly improved the oxidation rate and mineralization degree of both homogeneous Fenton-like oxidation and CWPO, achieving almost 90% TOC reduction after 1 h at stoichiometric H_2O_2 dose, 100 mg L^{-1} initial chlorophenol concentration, 1 g L^{-1} $\text{Fe}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst, pH 3 and 90°C temperature. Both $\text{Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ catalysts suffered fairly low iron leaching (<5%) and a remarkable stability in a three-cycles test with 2,4,6-TCP. The use of the magnetic catalyst is preferable due to its easy separation and recovery from the liquid phase by a magnet. Its magnetic properties remained unchanged after use in CWPO.

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1. Introduction

Chlorophenols (CPs) are widely used in the production of herbicides, fungicides, insecticides, pharmaceuticals and dyes.

The wastewater from those industries commonly contains chlorophenols in significant amounts, and they have been detected in both surface and ground waters [1–4]. This fact involves a significant risk for the environment due to the high toxicity, persistence and low biodegradability of these compounds which have been listed as priority pollutants by the European Decision 2455/2001/EC and by the US EPA in the Clean Water Act.

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Biological processes are ineffective for the removal of such recalcitrant compounds from wastewater requiring long acclimation periods [5,6]. Although thermal destruction is effective for the breakdown of CPs this way suffers from serious drawbacks derived from energy consumption and the formation of even more toxic species [7,8]. Activated carbon adsorption has also been used for the treatment of chlorophenols [9,10], but it leaves spent carbon as a waste of hazardous character. Therefore, considering other destructive technologies for the treatment of CPs is of significant interest. In this sense, Advanced Oxidation Processes (AOPs) appear to be a promising solution, which has been reported to be effective for CPs breakdown even at near-ambient temperature and pressure.

The Fenton process is one of the most commonly used AOP for the removal of recalcitrant pollutants from wastewaters [11–14]. It has gained large attention due to the simplicity of design and setup, safe operation, high efficiency and the use of readily availability reagents. However, the efficiency of this process is marred by the sludge generation since the catalyst, $\text{Fe}^{2+}/\text{Fe}^{3+}$ in solution, cannot be retained in the process requiring additional separation steps. Another drawback of the Fenton process is related to the costly consumption of H_2O_2 . The possibility of lowering the H_2O_2 dose for the purpose of reducing costs is limited. In fact, it has been recently demonstrated that the use of substoichiometric amounts of H_2O_2 in the oxidation of CPs leads to the formation of highly toxic condensation by-products such as chlorinated diphenyl ethers, biphenyls, dibenzofurans or dioxins [15–17]. The intensification of the process by increasing the temperature has proved to allow a more efficient use of H_2O_2 upon enhanced generation of OH radicals at low iron concentrations [18]. However, the need of dealing with the sludge generated in the process is not avoided. In this sense, the use of solid catalysts by immobilization of iron over a convenient support, the so-called Catalytic Wet Peroxide Oxidation (CWPO), offers a potential solution. So far, activated carbon [19,20], silica [21], mesostructured materials [22–24], zeolites [25,26], pillared clays [27–30] and alumina [31,32] have been used as supports to prepare the catalysts. Among them, the one based on alumina has proved to be an excellent highly-stable catalyst for CWPO not only with phenol but with real wastewaters from the cosmetic industry [31,32].

Typically, CWPO is conducted in a suspension of powdered particles. Therefore, an additional separation step is required to recover the catalyst from the reaction medium. This poses a major drawback for the application of CWPO for wastewater treatment. One approach for overcoming this drawback is to develop a magnetic catalyst that can be easily separated by an external magnet, thereby simplifying its recovery. Moreover, the use of magnetite as active phase represents an important advantage with respect to the conventional catalysts, commonly based on Fe_2O_3 , since it contains both Fe (II) and Fe (III) in its structure thus enhancing the rate of $\cdot\text{OH}$ generation. In a previous contribution we focused on the preparation and characterization of a magnetic $\text{Fe}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst, which showed to be more active than the conventional $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst and exhibited a high stability working under moderate conditions (50 °C) [33]. In this work, different oxidation strategies have been investigated for the treatment of chlorophenols with the aim of improving the treatment performance in terms of mineralization, remanent by-products and kinetics. Since the recalcitrant character of chlorophenols increases with the number of chlorine atoms in the phenolic ring, the oxidation of mono-, di- and tri- chlorophenols has been studied. Those strategies were homogeneous Fenton-like (Fe^{3+}) oxidation and CWPO with two different own-prepared $\text{Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ catalysts. The intensification of these processes by increasing the temperature has been analyzed on the basis of kinetics and mineralization degree of the organic species, namely TOC reduction. Particular attention has been paid to the formation of condensation by-products and the reaction mechanism. The reusability of the own-prepared catalysts has been evaluated as well.

2. Materials and methods

2.1. Catalysts preparation and characterization

Two γ -alumina-supported iron catalysts ($\text{Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$) were prepared. They were synthesized by incipient wetness impregnation of powdered $\gamma\text{-Al}_2\text{O}_3$ ($d_p < 100 \mu\text{m}$) supplied by Merck with a $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ aqueous solution. The Fe load was adjusted to a nominal 4% (w/w). After impregnation, the samples 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_2 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 $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ and $\text{Fe}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ for the non-magnetic and the magnetic catalyst, respectively.

X-ray diffraction (XRD) and Mössbauer techniques were used to determine the crystalline phases in the catalysts. The Mössbauer analysis has been described in detail elsewhere [33] and the X-ray diffraction profiles were obtained using a Siemens model D-5000 diffractometer with $\text{Cu K}\alpha$ radiation. These analyses allowed to confirm that iron were in the form of hematite in the $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst and magnetite in the $\text{Fe}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst. Total iron content was analyzed by inductively coupled plasma (ICP-MS Elan 6000 Perkin-Elmer Sciex) and the porous structure of the fresh and used catalysts was characterized from the nitrogen adsorption-desorption isotherms at 77 K (Micromeritics Tristar 3020). Elemental analyses 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. Magnetic measurements were performed in 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. Oxidation experiments

Oxidation runs were carried out in a 500 mL glass batch reactor equipped with a PTFE stirrer (700 rpm). All the experiments were performed adjusting the initial pH value of the reaction medium to 3 with nitric acid. Chlorophenols with different chlorine content (4-CP, 2,4-DCP and 2,4,6-TCP) were used as target pollutants. A 100 mg L^{-1} starting concentration of chlorophenol and the theoretical stoichiometric amount of H_2O_2 for complete oxidation up to CO_2 , H_2O and HCl , were always used. Homogeneous Fenton-like experiments were conducted at $10 \text{ mg L}^{-1} \text{Fe}^{3+}$, while CWPO was always carried out with $1 \text{ g L}^{-1} \text{Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ catalyst. Both established as the optimum values in previous works [18,33]. The temperature effect was tested within the 50–90 °C range.

A previous set of experiments with the three chlorophenols tested was conducted in absence of H_2O_2 within the range of temperatures studied (50–90 °C), confirming the very low adsorption of chlorophenols by the $\text{Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ catalysts prepared in this work (<5%).

2.3. Analytical methods

The progress of the oxidation processes was followed by periodically withdrawing and analyzing liquid samples from the reactor. In the case of CWPO experiments, the catalyst was separated by filtration using a PTFE filter (pore size $0.45 \mu\text{m}$). Chlorophenols were quantified by means of high-performance liquid chromatography (HPLC; Varian Pro-Start 325) equipped with 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

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