



Degradation of diphenhydramine by photo-Fenton using magnetically recoverable iron oxide nanoparticles as catalyst



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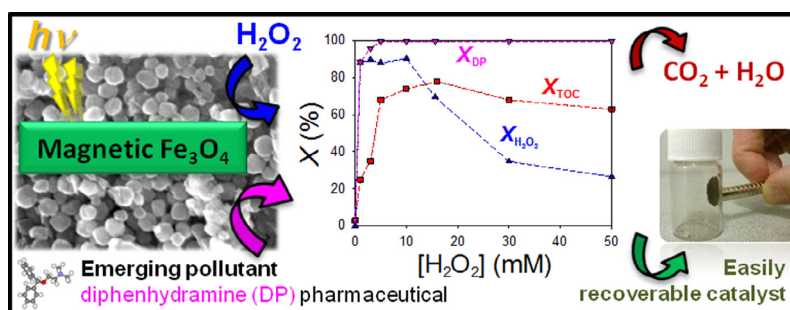
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HIGHLIGHTS

- Magnetic iron oxide catalysts (50–100 nm) synthesized by the solvothermal method.
- Diphenhydramine emerging pollutant completely degraded by photo-Fenton process.
- Iron species leachate into water solutions below the European Directives thresholds.
- Catalyst easy recover and reuse by magnetic separation.

GRAPHICAL ABSTRACT



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ABSTRACT

Iron oxide nanoparticles, with size ranging from 50 to 100 nm, were synthesized by a solvothermal method. The amounts of iron(III) chloride precursor (from 2.5 to 10.0 mmol) and sodium hydroxide (between 10 and 30 mmol) were varied along with the synthesis temperature (180 or 200 °C). Depending on the synthesis conditions, samples with magnetic properties consisting of magnetite (Fe_3O_4), or by a mixture of magnetite and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and samples with no magnetism consisting of hematite ($\alpha\text{-Fe}_2\text{O}_3$), were obtained.

The catalytic activity of the materials was studied for the degradation of diphenhydramine using the photo-Fenton process. All materials performed well on the degradation of this emerging pollutant. The best compromise between catalytic activity and stability was obtained with pure magnetite nanoparticles prepared at 180 °C from a 4:1 molar ratio between sodium hydroxide and iron(III) chloride. This catalyst was used in further studies at different pH (2.8–11.0), catalyst loads (up to 200 mg L^{-1}) and hydrogen peroxide concentrations (1–50 mM). Complete degradation of diphenhydramine with 78% of mineralization was achieved at relatively low leaching of iron species from the catalyst to the aqueous solution (1.9 mg L^{-1}). Acidic pH (2.8) is preferable to neutral or alkaline pH (i.e. 6.0, 7.0 and 11.0) resulting from the higher efficiency of H_2O_2 to promote the formation of hydroxyl radicals under those conditions. Complete degradation of the pollutant can be obtained at acidic pH even at very low catalyst load (20 mg L^{-1}). The use of stoichiometric H_2O_2 concentration allows for complete diphenhydramine conversion, maximum mineralization, and leaching of iron complying with European Directives. From recovery and reutilization experiments it was found that the selected magnetic catalyst might be easily recovered by magnetic separation, showing good stability and reusability properties.

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1. Introduction

The importance of magnetic nanoparticles has grown in almost all fields and, more recently, the use of iron oxides nanoparticles has been extensively investigated in environmental applications [1]. Magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are the most common forms of magnetic iron oxide nanoparticles in nature, and they can be easily synthesized by co-precipitation [2,3], thermal decomposition [4] or hydrothermal/solvothermal [5] methods. These nanomaterials become superparamagnetic when their particle size is below a critical value (typically 50 nm), and are known as superparamagnetic iron oxide nanoparticles (SPIONs) [6]. The application of SPIONs as catalysts in water cleanup have attracted increasing attention due to their high surface area, uniform pore size distribution and convenient separation from solution by an external magnetic field. Indeed, these materials can overcome two of the main limitations found when using catalysts without magnetic properties: (i) difficult separation by filtration processes in the case of powder catalysts and (ii) decrease of activity when nanoparticles are immobilized on rigid substrates [1,7,8].

Advanced oxidation processes (AOPs) are known as relatively low cost, easy to operate and effective options for water purification and waste water treatment, and they can be coupled with biological or traditional physicochemical processes in order to design cost-effective solutions. Among the existing AOPs, the Fenton process (named after the Fenton's reaction following the 1894 studies of Henry Fenton [9]) consists on the production of highly reactive hydroxyl radicals ($\text{HO}\cdot$) from a mixture of hydrogen peroxide (H_2O_2) and Fe^{2+} ions at acidic pHs (2.5–3.0). This process can be assisted with ultraviolet and/or visible light (known as photo-Fenton process) to accelerate the regeneration/reduction of Fe^{3+} into Fe^{2+} and restart the normal cycle of the Fenton reaction. In fact, the photo-Fenton process has proven to be a promising alternative for the degradation of a large number of hazardous water pollutants [10]. Nevertheless, this process has some disadvantages such as the production of sludge and the difficult recovery of the catalyst, which is often mandatory due to the maximum dissolved iron concentration allowed in European Union standards for discharge of treated waters, namely 2.0 mg L^{-1} (as defined by the Portuguese legislation, Decreto-Lei 236/98) while for drinking water is 0.2 mg L^{-1} [11].

Magnetic nanoparticles have been already used in different AOPs. For instance, a titanium dioxide/magnetite catalyst was used for mineralization of sucrose in photocatalysis [12], a silicon dioxide/magnetite catalyst was used for degradation of Reactive Black 5 in catalytic ozonation [13], while magnetite, maghemite and nickel ferrite materials were used for the treatment of different model pollutants by Fenton and photo-Fenton processes, including aniline [7], phenol [14], phenolic derivatives [8,15,16] and azo dyes such as rhodamine B, methylene blue and methyl orange [8,17].

The pharmaceutical compound, diphenhydramine (DP), has been used in our group as model pollutant to study the photocatalytic efficiency of TiO_2 -carbon based materials, under both UV-Vis and visible light irradiation [18–21], since it has been recognized the importance to remove pharmaceutical-derived emerging contaminants, such as DP [22,23], from water effluents using AOPs [24]. However, to the best of our knowledge, studies on the photo-Fenton degradation of this important pharmaceutical were not reported yet, in particular when using magnetic nanoparticles. In the present work, iron oxide nanoparticles were synthesized and tested for the degradation of DP by the photo-Fenton process, aiming the optimization of the photo-Fenton operating conditions and a comprehensive study of the catalytic properties of the magnetically recoverable materials.

2. Experimental

2.1. Chemicals

Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, >99.5%), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, >99.0%), sodium hydroxide (NaOH, >99%), potassium hydroxide (KOH, >90%), sulfuric acid (H_2SO_4 , $\geq 99.7\%$), diphenhydramine hydrochloride (2-(diphenylmethoxy)-N,N-dimethylethylamine hydrochloride, 99%), H_2O_2 (30% w/w) and 1,10-phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2$, >99%), were obtained from Sigma-Aldrich. Iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, >99.5%) was supplied by Merck.

2.2. Catalysts synthesis and characterization

The magnetic nanoparticles of iron oxide used in this study were synthesized by a solvothermal method, adapting methodologies described in the literature [25]. In a typical procedure, 5.0 mmol of the precursor (FeCl_3) was dissolved in 20 mL of ethylene glycol, and then 20 mmol of NaOH was added to the resultant mixture. Thereafter, the mixture obtained was placed in a Teflon vessel inside a stainless steel reactor (Parr Acid Digestion Vessel, Model 4748) and heated at 180°C for 6 h. After the heat exposure time, the mixture was allowed to cool down to room temperature and withdrawn from the reactor. The synthesized solid material was recovered by vacuum filtration, followed by washing with water and drying at 40°C for 24 h. This procedure was repeated for each synthesized sample, yielding ultimately six different types of nanoparticles (samples S1–S6), by varying the amount of precursor (between 2.5 and 10.0 mmol of FeCl_3), the amount of NaOH (between 10 and 30 mmol) and the synthesis temperature (180 or 200°C), as summarized in Table 1.

The synthesized catalysts were characterized by X-ray diffraction (XRD) in a Philips PW 1710 equipment and by scanning electron microscopy (SEM) in a FEI Quanta 400FEG ESEM/EDAX Genesis X4M instrument, equipped with energy dispersive spectroscopy (EDS).

2.3. Photo-Fenton experiments and analytical procedures

The photo-Fenton experiments were performed in a quartz cylindrical reactor filled with 7.5 mL of a 100 mg L^{-1} ($3.40 \times 10^{-4} \text{ M}$) aqueous solution of DP at room temperature (25°C). The UV-Vis light irradiation source consisted of a Heraeus TQ 150 medium-pressure mercury-vapor lamp. A DURAN® glass cooling jacket with water recirculation was used to operate in the near-UV/Vis light ($\lambda > 350 \text{ nm}$) and to control the operational temperature. The amount of irradiance entering the photoreactor was equal to 33 mW cm^{-2} .

In a typical experiment the suspension was magnetically stirred in dark and purged with oxygen flow until the stabilization of both temperature and pH (ca. 30 min). Time zero for reaction takeoff was defined as the time when the lamp was turned-on and H_2O_2 simultaneously added. The experiments were performed at varying pHs (from 2.8 to 11.0, by adding H_2SO_4 or KOH solutions), catalyst loads (20 – 200 mg L^{-1}) and H_2O_2 dosages (1 – 50 mM).

The concentration of DP was monitored by high-performance liquid chromatography (HPLC) with a Hitachi Elite LaChrom system equipped with a Hydrosphere C18 column ($250 \text{ mm} \times 4.6 \text{ mm}$; $5 \mu\text{m}$ particles), a diode array detector (L-2450) and a solvent delivery pump (L-2130). Total organic carbon (TOC) was determined for selected samples at the end of the experiments using a Shimadzu TOC-5000A analyzer. H_2O_2 concentration was determined by adding 1 mL of a 0.5 M H_2SO_4 solution and 0.1 mL of $\text{TiO}(\text{SO}_4)$ (15 wt.% in diluted H_2SO_4) to 1 mL of the liquid sample,

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