Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Hybrid magnetic graphitic nanocomposites for catalytic wet peroxide oxidation applications

Rui S. Ribeiro[a], Adrián M.T. Silva[b], Pedro B. Tavares[c], José L. Figueiredo[b], Joaquim L. Faria[b], Helder T. Gomes[a,*]

[a] *Laboratory of Separation and Reaction Engineering–Laboratory of Catalysis and Materials (LSRE-LCM), Departamento de Tecnologia Química e Biológica, Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal*
[b] *Laboratory of Separation and Reaction Engineering–Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*
[c] *CQVR—Centro de Química–Vila Real, Escola de Ciências da Vida e do Ambiente, Universidade de Trás-os-Montes e Alto Douro, 5000-801 Vila Real, Portugal*

ARTICLE INFO

Article history:
Received 29 January 2016
Received in revised form 22 April 2016
Accepted 27 April 2016
Available online xxx

Keywords:
Magnetic nanoparticles (MNP)
Core-shell nanocomposites
Catalytic wet peroxide oxidation (CWPO)
Heterogeneous Fenton process

ABSTRACT

Fe_3O_4, with a lattice parameter a = 8.357 Å and average particle size of 12.5 ± 3.6 nm, was successfully encapsulated within a graphitic structure by a hierarchical co-assembly approach, followed by thermal annealing. The resulting material was denoted as MGNC—magnetic graphitic nanocomposite. MGNC possesses average core size of 109 ± 35 nm (mainly composed by agglomerates of magnetic nanoparticles), stability up to 400 °C under oxidizing atmosphere, a micro-mesoporous structure with a fairly developed specific surface area ($S_{BET} = 330\ m^2\ g^{-1}$) and neutral character ($pH_{PZC} = 7.1$).

Catalytic wet peroxide oxidation (CWPO) experiments performed with a 4-nitrophenol (4-NP)/Fe_3O_4 mass ratio fixed at 36.6, allowed to achieve high efficiency of catalyst usage throughout the wide range of 4-NP concentration considered ($200\ mg\ L^{-1}$–$5\ g\ L^{-1}$). The inclusion of Fe_3O_4 nanoparticles in a graphitic structure during the synthesis of MGNC was found to (i) enhance the catalytic activity in CWPO when compared to Fe_3O_4, due to increased adsorptive interactions between the surface of the catalyst and the pollutant molecules, while (ii) strongly limiting the leaching of Fe species from Fe_3O_4 to the treated water, due to the confinement effect caused by the carbon shell.

As a result of these effects, unprecedented pollutant mass removals were obtained – ranging from $5000\ mg\ g^{-1}\ h^{-1}$, when the CWPO process is performed with $[4\text{-NP}]_0 = 200\ mg\ L^{-1}$ at pH = 3, to $1250\ mg\ g^{-1}\ h^{-1}$, when $[4\text{-NP}]_0 = 5\ g\ L^{-1}$. High efficiency of H_2O_2 consumption is obtained when MGNC is applied in the CWPO of 4-NP solutions at pH = 3, with TOC removals per unit of H_2O_2 decomposed (η_{H2O2}) in the range 64–100%. In addition, the MGNC catalyst is also active at pH = 6; in this case a pollutant mass removal of $2090\ mg\ g^{-1}\ h^{-1}$ was obtained.

Although MGNC partially deactivates through successive reusability cycles, the pollutant mass removal obtained at the end of the fourth cycle is still very high when $200\ mg\ L^{-1}$ 4-NP solutions are considered ($4808\ mg\ g^{-1}\ h^{-1}$, representing only a ca. 4% decrease when compared to the first cycle). A higher deactivation of the MGNC catalyst is observed when $5\ g\ L^{-1}$ 4-NP solutions are employed. Nevertheless, the pollutant mass removal obtained at the end of the third cycle is still high ($551\ mg\ g^{-1}\ h^{-1}$).

1. Introduction

The development of efficient and economically viable treatment technologies, able to cope with the increasing complexity of industrial wastewaters, is an ongoing challenge for the scientific community. In particular, toxic and refractory compounds like phenols and nitrophenols – often found in industrial wastewaters, such as those from pharmaceutical, petrochemical, metallurgical, textile, rubber and plastic industries, refineries, fungicides and even from municipal landfill leachates [1–6] – can have a negative impact on conventional biological wastewater treatment processes. Therefore, other treatment options should be considered. In this context, the so-called advanced oxidation processes (AOP) are usually seen as a powerful tool [7], since they rely on the formation of highly oxidizing hydroxyl radicals, $HO^{\bullet}$ (standard reduction potential between +2.8 V and +2.0 V at pH 0 and 14, respectively), which serve

---

* Corresponding author.
E-mail address: htgomes@ipb.pt (H.T. Gomes).

http://dx.doi.org/10.1016/j.cattod.2016.04.040
0920-5861/

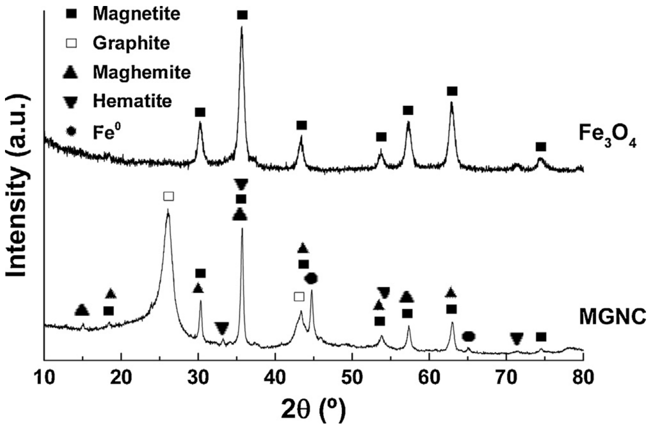

Fig. 1. XRD diffraction patterns of Fe_3O_4 and MGNC.

as effective species for the destruction of a huge range of refractory organic pollutants [8,9].

Catalytic wet peroxide oxidation (CWPO) is an AOP characterized by the formation of $HO^•$ radicals from the catalytic decomposition of hydrogen peroxide (H_2O_2) performed at low temperature and atmospheric pressure [10,11]. Therefore, CWPO is widely recognized as a low cost AOP [11,12]. However, as recently reviewed, further optimization of catalyst design is still required in order to bring CWPO to the forefront of the most efficient AOP technologies [13]. In this context, very different carbon-based nanostructured composites containing metallic nanoparticles have been recently applied with success in CWPO [14–16], their improved catalytic performance being ascribed to several synergistic effects that arise from the combination of the high catalytic activity of iron, or other metal species, with the easily tunable properties of carbon-based materials [13]. Furthermore, the magnetic properties of these catalysts may allow the implementation of in situ magnetic separation systems for catalyst recovery after reaction, which would be an additional advantage to the process. Bearing this in mind, hybrid magnetic carbon composites may be considered the next step in the evolution of catalysts for CWPO [13]. In the light of these findings, a hybrid magnetic graphitic nanocomposite (MGNC) material was synthesised in the present work by hierarchical co-assembly of magnetic nanoparticles and carbon precursors, followed by thermal annealing. After a detailed characterization, the performance of MGNC in the CWPO of refractory organic pollutants was evaluated using 4-nitrophenol (4-NP) as model pollutant, in a very wide concentration range (200 mg L^{-1}–5 g L^{-1}). In order to optimize the efficiency of catalyst usage, the MGNC catalyst dosage was kept very low when compared to the pollutant concentration, with a fixed pollutant/catalyst mass ratio as high as 10.

2. Materials and methods

2.1. Magnetite nanoparticles

Magnetite (Fe_3O_4) was synthesised by co-precipitation of Fe^{2+} and Fe^{3+} in basic solution, at 30 °C and under N_2 atmosphere, adapting a procedure described elsewhere [17]. For that purpose, 13.44 mmol of iron (II) chloride tetrahydrate and 26.88 mmol of iron (III) chloride hexahydrate were dissolved in 250 mL of distilled water and transferred into a 500 mL glass reactor, equipped with a condenser and immersed in an oil bath with controlled temperature. When the desired temperature was reached, the mixture was deaerated during 10 min with N_2 under vigorous stirring, and further kept under inert atmosphere. At this point, 10 mL of ammonium hydroxide solution (25 wt.%) were quickly added, a black precipitate being instantly obtained. Afterwards, possible residues of the precursors were washed-out with distilled water, the sample being then dried in an oven at 60 °C for 24 h, resulting in the Fe_3O_4 material.

2.2. Hybrid magnetic graphitic nanocomposites

The magnetic graphitic nanocomposite (MGNC) material was prepared by hierarchical co-assembly of Fe_3O_4 nanoparticles and carbon precursors, followed by thermal annealing, adapting the procedure described elsewhere [18]. For that purpose, 5 g of copolymer pluronic F127 was dissolved in 50 mL of H_2O, in a round bottom 500 mL glass reactor equipped with a condenser and immersed in an oil bath with temperature control. Then, 5 mL of Fe_3O_4 suspension (17 mg mL^{-1}, previously obtained by dispersion of Fe_3O_4 in H_2O in an ultrasonic bath) were added, the resulting solution being stirred during 2 h at 66 °C for homogenization. After that, ≈ 60 mL of a phenol/formaldehyde resol solution were added, the resulting mixture being kept under stirring (400 rpm) at 66 °C for 72 h and then at 70 °C for an additional 24 h. The phenol/formaldehyde resol solution was prepared by dissolution of 2.0 g of phenol in 7.0 mL of formaldehyde 37 wt.% solution, to which 50.0 mL of NaOH 0.1 mol L^{-1} were added, the solution being then kept under stirring at 70 °C for 30 min.

The recovered solids were washed with distilled water in order to promote the wash-out of some possible residues of the precursors and then dried overnight in an oven at 60 °C. Afterwards the sample was thermally annealed under a N_2 flow (100 cm^3 min^{-1}) at 120 °C, 400 °C and 600 °C during 60 min at each temperature and then at 800 °C for 240 min, defining a heating ramp of 2 °C min^{-1}. Finally, the sample was washed with 1 L of distilled water at 50 °C under vacuum filtration, and then with 1 L of HCl solution (pH = 3), also at 50 °C under vacuum filtration, being afterwards dried overnight in an oven at 60 °C, resulting in the MGNC material.

2.3. Characterization techniques

X-ray diffraction (XRD) analysis was performed in a PANalytical X'Pert MPD equipped with a X'Celerator detector and secondary monochromator (Cu Kα $\lambda = 0.154$ nm; data recorded at a 0.017° step size). Highscore Plus and PowderCell software's were used to identify the crystallographic phases present and to calculate the crystallite sizes from Rietveld refinement of the XRD diffraction patterns. Transmission electron microscopy (TEM) was performed in a LEO 906E instrument operating at 120 kV, equipped with a 4 Mpixel 28 × 28 mm CCD camera from TRS. 110 counts were performed for the determination of Fe_3O_4 particle size; 70 counts were performed for the determination of the metal core size of the MGNC catalyst. Textural characterization was performed in a Quantachrome NOVA 4200e adsorption analyser. Thermogravimetric analysis (TGA) was performed using a Netzsch STA 409 PC equipment under oxidative atmosphere. The pH of point of zero charge (pH_{PZC}) was determined by pH drift tests [19].

2.4. Catalytic wet peroxide oxidation experiments

Batch CWPO experiments were performed in a well-stirred (600 rpm) glass reactor equipped with a condenser, a temperature measurement thermocouple, a pH measurement electrode and a sample collection port. The reactor was loaded with 4-NP aqueous solutions (in the range 200 mg L^{-1}–5.0 g L^{-1}) and heated by immersion in an oil bath at controlled temperature. Upon stabilization at 80 °C, the solution pH was adjusted (in the range pH 3–9) by means of H_2SO_4 and NaOH solutions, and the experiments were allowed to proceed freely, without further conditioning of pH. A

Please cite this article in press as: R.S. Ribeiro, et al., Hybrid magnetic graphitic nanocomposites for catalytic wet peroxide oxidation applications, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.04.040