HYBRID MAGNETIC NANOPARTICLES FOR WET PEROXIDE OXIDATION OF PARACETAMOL

Arnaldo V. Dias[a,b], Adriano S. Silva[a,c,d*], Fernanda F. Roman[a,c,d], Ana P. Ferreira da Silva[a], Jose L. Diaz de Tuesta[a,e], Ana M. Ferrari Lima[b], Helder T. Gomes[a]

[a]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, 5300-253 Bragança, Portugal.

[b]Universidade Tecnológica Federal do Paraná, Campus Apucarana, 86812-460 Apucarana, Brazil.

[c]Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculty of Engineering, University of Porto, 4200-465 Porto, Portugal

[d]Associate Laboratory in Chemical Engineering (ALiCE), Faculty of Engineering, University of Porto, 4200-465 Porto, Portugal

[e]Department of Chemical and Environmental Technology, ESCET, Rey Juan Carlos University, Tulipán s/n, 28933 Móstoles, Spain

**E-mail: adriano.santossilva@ipb.pt*

Resumo

A performance de nanopartículas de ferrite de cobalto, ferrite de cobalto recoberta por carbono preparada por uma metodologia tradicional e ferrite de cobalto preparada por metodologia verde foi avaliada na remoção de paracetamol (PCM), escolhido como poluente modelo, por um processo de oxidação húmida com peróxido de hidrogénio (CWPO). O núcelo magnético foi sintetizado por sol-gel, e na metodologia tradicional de recobrimento de carbono foi considerado resorcinol/formaldeído como precursores de carbono, enquanto que na metodologia verde foi considerado phloroglucinol/ácido glioxílico. Todas as nanopartículas magnéticas (NPMs) apresentaram atividade na remoção de PCM por CWPO. Ambas as NPMs recobertas com carbono apresentaram resultados melhores que o núcleo não recoberto, devido à presença da camada de carbono à volta do núcleo, que também tem atividade pelas propriedades eletrónicas do recobrimento de carbono. O catalisador recoberto pela metodologia verde possui uma decomposição de peróxido de hidrogénio mais controlada. O teste de reutilização do catalisador mostrou a estabilidade do material, com perfis de concentração similares e uma remoção de PCM mais rápida que na primeira utilização.

Palavras chave: Nanopartículas magnéticas híbridas, poluente orgânico, paracetamol, tratamento de águas residuais, oxidação húmida com peróxido de hidrogénio

Abstract

The performance of non-coated magnetic nanoparticle (MNPs) based on cobalt ferrite ($CoFe_2O_4$), and of carbon-coated cobalt ferrite prepared by a traditional method ($CoFe_2O_4$@C1), and by a greener method ($CoFe_2O_4$@C2) was assessed in the removal of paracetamol (PCM), used as model pharmaceutical pollutant, by catalytic wet peroxide oxidation (CWPO). The magnetic core was synthesized by sol-gel methodology, and the traditional method for carbon coating considered resorcinol and formaldehyde as carbon precursors. In contrast, the greener method was performed considering phloroglucinol and glyoxylic acid as carbon precursors. All MNPs presented activity on the removal of PCM by CWPO. Both carbon-coated MNPs overcome the results obtained with the bare core, due to the carbon layer covering the core, which can also have catalytic activity. The catalyst coated by the greener method ($CoFe_2O_4$@C2) shows a more controlled decomposition of hydrogen peroxide. A reutilization test performed to evaluate the stability of this catalyst showed complete removal of PCM faster than in the first usage, with a similar concentration trend profile in both repetitions.

Keywords: Hybrid magnetic nanoparticles, organic pollutant, paracetamol, wastewater treatment, catalytic wet peroxide oxidation.

1. Introduction

Water is a critical natural resource, with a wide impact on human life[1]. The supply of clean water has great environmental, social and economic effects, especially for developing countries that constantly face issues of freshwater supply [2]. For instance, about 74% of the world population had access to drinking water in 2020. The constant growth of people in cities and the rapid development of the industry are the main vectors driving the widespread contamination of surface waters and groundwaters with pollutants, such as pathogens, heavy metals and organic pollutants [3].

Pollution with organic contaminants has received increasing attention due to widespread detection of their presence in surface and ground waters. Among pollutants, pharmaceutically active compounds (PhACs) deserve special attention due to their harmful effects at low concentration on aquatic life. Their ubiquitous presence in water threatens public health, since conventional treatments used in wastewater treatment plants fail to properly remove them from water [4]. Public authorities have also noticed the importance of wastewater treatment for sustainable development with one specific UN Sustainable Development Goal (SDG) for clean water and sanitation, SDG 6. Target 6.3 states that “By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally”. Despite public awareness of the relevance of this theme, indicators demonstrate that the current situation is critical, and concerns are only increasing.

Considering the importance of potable water for the development of all countries and the concerns regarding the viability of meeting environmental standards of water quality, there is a clear need to develop innovative solutions. More cost-efficient methods and materials are required despite the increasing report of new methodologies and strategies to tackle this problem [3]. From this perspective, catalytic wet peroxide oxidation (CWPO) is a wastewater treatment that showed promising results in removing organic pollutants from wastewaters[5]. In this technology, the interaction of H_2O_2 with a suitable catalyst can lead to the formation of hydroxyl radicals, which are known to be highly oxidizing species. The typical catalysts used in CWPO generally comprise a transition metal in its structure. Carbon-based materials have also demonstrated activity in this process, mostly associated with its redox capacity to exchange electrons and ability for the efficient decomposition of hydrogen peroxide into hydroxyl radicals.

Metal-based catalysts often have issues related to the leaching of the metal used as active phase, and carbon-based catalysts usually have less activity than metal-based ones. To overcome these drawbacks, carbon-coated metal oxides (hybrid materials) could be a good solution for materials used as catalysts. Furthermore, the diverse range of methodologies to prepare iron oxide nanoparticles enables the use of nanotechnology in this field. Nanoparticles have several advantages compared with traditional macro and micro materials due to their unique physical and chemical properties [6].

Therefore, in this work bare cobalt ferrite and carbon-coated cobalt ferrite were considered to remove paracetamol, chosen as a model organic pollutant, from a simulated matrix by CWPO. The magnetic inorganic core was prepared by sol-gel methodology, and carbon-coating was performed considering 2 procedures, one described in previous works [7] and another by a greener strategy.

2. Experimental

2.1 Reagents

Iron (III) chloride hexahydrate (99%, Merck), cobalt (II) chloride hexahydrate (99%, Fisher Chemical), ethylene glycol (99.5%, Fluka Analytical) and ethanol absolute (99.8%, Fisher Scientific) were used for the synthesis of the magnetic core. Tetraethyl orthosilicate (TEOS, 98%, Fluka), resorcinol (99%, Fisher Scientific), formaldehyde (37-38% wt., Panreac), glyoxylic acid monohydrate (98%, Sigma Aldrich), phloroglucinol (99%, Sigma Aldrich) were used for the coating of the MNPs. Sodium hydroxide (99.1%, Fisher Scientific) was used to remove the silica content. The oxidation runs were performed using paracetamol (98%, Alfa Aesar), hydrogen peroxide (30% w/v, Fisher Chemical) and sulfuric acid (98%, Panreac). For the analytical techniques, ortho-phosphoric acid (85%, Riedel-de Haen), titanium (IV) oxysulfate (15 wt% in dilute sulfuric acid 99.99%) and sodium sulfite (97%, Sigma Aldrich) were considered.

2.2 Synthesis of hybrid nanoparticles

Hybrid nanoparticles were prepared in different steps: i) synthesis of the magnetic core, ii) coating, iii) annealing, and iv) etching. Cobalt ferrite was prepared by a sol-gel method described in another work [8]. Briefly, Fe (III) and Co (II) solutions in ethylene glycol and ethyl alcohol were mixed with a molar ratio of 1:2. The resultant solution was heated for 2 h at 60 °C and then at 189 °C until it became a gel and dried to the final solid. The recovered solid was thermal treated in air muffle at 300 °C for 24 h and at 600 °C for 12 h to remove organic impurities from sol-gel and obtain purified $CoFe_2O_4$ crystals.

For coating step, 0.25 g of magnetic core was sonicated with 150 mL of absolute ethanol and 50 mL of water to ensure the dispersion of the nanoparticles in the liquid media. After that, the solution was transferred to a round-bottom flask previously loaded with 0.1 g of resorcinol and 1.2 mL of a 28% ammonia solution. The flask was heated to 30 °C for 1 h with stirring until 210 µL of TEOS and 150 µL of formaldehyde were added. The media was kept at 30 °C for 6 h and then it was heated to 80 °C for 8 h. The final solid was recovered and washed several times until rinsing waters reached neutral pH and dried in an air oven overnight at 60 °C. The final material was named $CoFe_2O_4$@resin1. Resorcinol and formaldehyde were changed for phloroglucinol and glyoxylic acid to make the methodology greener in the second approach. All the steps were performed the same way, and the final nanoparticles were labelled as $CoFe_2O_4$@resin2.

Further to the coating process, the resin-coated nanoparticles went through carbonization under an inert atmosphere (N_2) in a tubular furnace (ROS 50/250/12, Thermoconcept). The thermal treatment was conducted at 120 and 400 °C for 1 h at each temperature and at 600 °C for 6 h. The resultant nanomaterial was recovered from the furnace and reserved for the final step and named $CoFe_2O_4$@C1.Si (previous $CoFe_2O_4$@resin1) and $CoFe_2O_4$@C2.Si (previous $CoFe_2O_4$@resin2). Etching was performed using 0.1 mL of NaOH 10 M solution per gram of nanoparticles. The system remained under stirring at room temperature for 16 h. In the end, the nanoparticles were recovered, washed until complete removal of the basic solution and dried in an air oven at 60 °C. Final nanoparticles were named $CoFe_2O_4$@C1 and $CoFe_2O_4$@C2.

2.3 Characterization techniques

The textural properties of the materials were determined from N_2 adsorption-desorption isotherms at 77 K, obtained in a Quantachrome instrument NOVA TOUCH LX^4 adsorption-analyser. The BET (Brunauer-Emmett-Teller) specific surface area (S_{BET}) was calculated in a range of p/p_0 0.05 – 0.35 and the total volume of pores was calculated considering p/p_0 0.98. FTIR spectra of the samples was recorded on a Perking Elmer FTIR spectrophotometer in UATR mode, with a resolution of 4 cm^{-1}.

2.4 Reaction runs and analytical techniques

Oxidation reactions were carried out with 100 mL of paracetamol solution (100 ppm) and the stoichiometric amount of H_2O_2 needed for its complete mineralization, 80 °C, and initial pH 3.5. After pouring the pollutant solution and hydrogen peroxide into a round bottom flask in an oil bath, the catalyst was added into the flask with a 2.5 $g{\cdot}L^{-1}$ catalyst concentration. Concentrations of PCM, H_2O_2 and aromatics were followed against time during 24 h, withdrawing samples (1 mL for each analysis) from the reaction media and using Na_2SO_3 to stop the reaction in the samples before further analysis to determine PCM concentration and aromatic compounds.

PCM and H_2O_2 concentrations were determined according to the procedure used in other works [9]. In brief, PCM concentration was followed by an analysis of reaction samples in HPLC, and H_2O_2 concentration was determined by UV/Vis spectrophotometry using a colorimetric method. The aromaticity throughout the reactions was analyzed according to a methodology described elsewhere [10]. The samples aliquot was diluted in a phosphate buffer solution at pH 7.0, and its absorbance determined by UV/vis spectrophotometry at a wavelength of 254 nm.

A non-catalytic run and adsorption experiments were done under the same operating conditions without catalyst and H_2O_2, respectively.

3. Results and discussion

3.1 Characterization

Nitrogen sorption isotherms of the carbon-coated magnetic nanoparticles ($CoFe_2O_4$@C1.Si and $CoFe_2O_4$@C2.Si) acid are shown in Figure 1. It can be seen that all materials show typical type IV isotherms with type H2 hysteresis, according to the classification established by IUPAC. This type of isotherm is given by mesoporous materials in which the adsorption behaviour is determined by the adsorbent-adsorptive interactions and the interactions between the molecules in the condensed state.

The result obtained shows the increase in surface area of the nanoparticle after the complete synthesis procedure. Moreover, the increase in surface area observed after etching represents the successful removal of silica from the nanoparticle, giving place to the formation of pores. The FT-IR spectroscopy results are represented in ***Figure 2***.

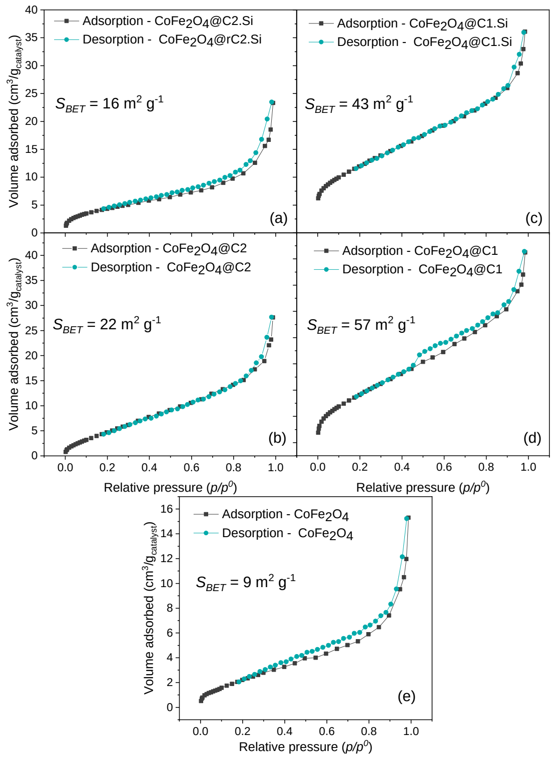

Figure 1. N_2 adsorption and desorption isotherms of the bare core (e), before (a and c), and after (b and d) etching.

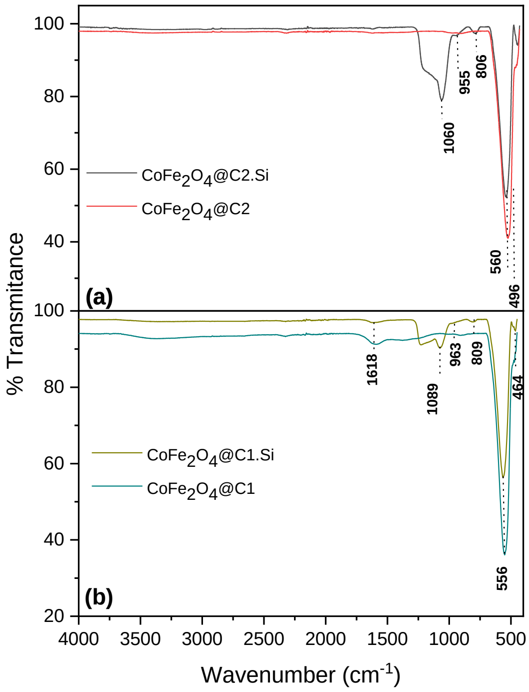

Figure 2. FTIR spectra of (a) materials prepared using phloroglucinol and glyoxylic acid and (b) resorcinol and formaldehyde.

The peaks between 460 and 500 cm^{-1} are attributed to the stretching vibration of octahedral sites, indicating the Co-O bond, while the peaks observed at a wavenumber around of 560 cm^{-1} are attributed to the tetrahedral sites of Fe-O bond, confirming the formation of $CoFe_2O_4$ in the materials [11]. A strong and wide absorption band around 1060 and 1089 cm^{-1} were also observed for $CoFe_2O_4$@C1.Si and $CoFe_2O_4$@C2.Si, which are attributable to Si-O-Si stretching vibrations, while the absorption bands around 800 and 960 cm^{-1} are assigned to Si-O symmetric stretching vibrations. The absence of these bands for the final nanoparticles is another evidence of silica removal after etching [12].

Normalized concentrations through reaction time for H_2O_2 and PCM are depicted in Figure 3 for the CWPO experiments.

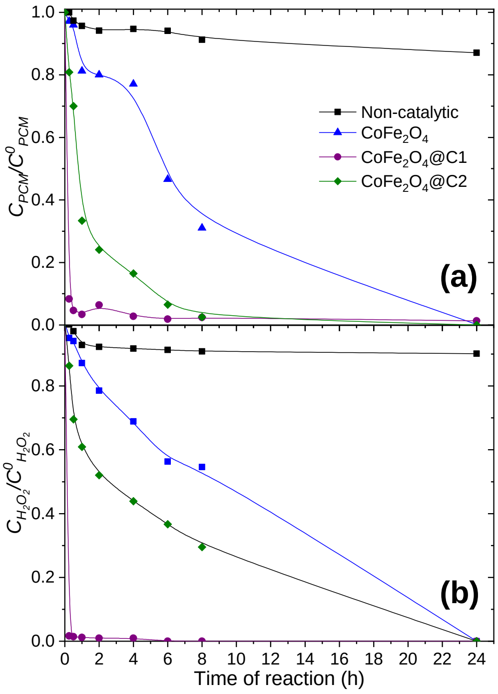

Figure 3. Normalized concentration of (a) PCM and (b) H_2O_2 (lines connecting points are only indicating trends). Operating conditions: $C_{PCM,0}$ = 100 mg·L^{-1}, $C_{H_2O_2,0}$ = 472.4 mg·L^{-1}, C_{cat} = 2.5 g·L^{-1}, pH_0 = 3.5 and T = 80 °C.

The non-catalytic run shows that the removal of contaminant and H_2O_2 decomposition are not significant, with 13% of pollutant removal and 10% of H_2O_2 decomposition after 24 h of reaction being obtained. In 8 h of reaction, both coated nanoparticles ($CoFe_2O_4$@C1 and $CoFe_2O_4$@C2) overcame the result obtained with the bare core ($CoFe_2O_4$). For instance, more than 90% of PCM was removed after 8 h of reaction with coated nanoparticles and around 70% with the uncoated magnetic core. The better performance observed for coated nanoparticles can be ascribed to the combined activity of the metal core and carbon coating, increasing pollutant removal, as well as to the higher interaction pollutant-catalyst due to adsorption. Adsorption runs showed removal of the pollutant of 4.5, 23.2 and 7.1% after 6 h for $CoFe_2O_4$, $CoFe_2O_4$@C1 and $CoFe_2O_4$@C2, respectively, confirming the higher interaction of the pollutant with the carbon-coated materials. Despite this, adsorption is not the driving agent for removing the pollutant since, in 6 h of reaction, all materials were able to remove more pollutant in the oxidation runs than in pure adsorption runs.

The degradation of PCM results in oxidized intermediate compounds formed in the reaction media. The measurement of the presence of aromatic compounds throughout time confirm the formation of oxidized intermediate compounds and consequent PCM oxidation, as shown in Figure 4.

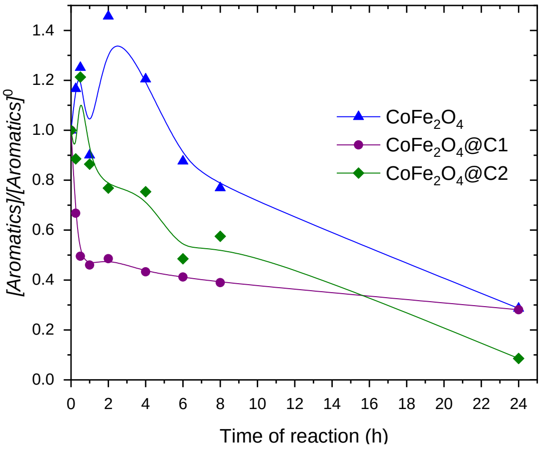

Figure 4. Aromaticity during CWPO experiments (lines connecting points are only indicating trends). Operating conditions: $C_{PCM,0}$ = 100 mg·L^{-1}, $C_{H_2O_2,0}$ = 472.4 mg·L^{-1}, C_{cat} = 2.5 g·L^{-1}, pH$_0$ = 3.5 and T = 80 °C.

The determination of aromatic shows that the reactions carried with $CoFe_2O_4$ and $CoFe_2O_4$@C2 as catalysts formed intermediate compounds in reaction times starting in 15 min. According to this analysis, the reaction carried out using $CoFe_2O_4$@C1 did not show the formation of intermediates. Despite the fast removal of pollutant observed for $CoFe_2O_4$@C1, the other coated nanoparticle could lower about 20% more of the aromatic compounds at the end of the reaction. For this reason, the catalyst with the best performance in the wastewater treatment by CWPO was $CoFe_2O_4$@C2.

The advantage of heterogeneous catalysis compared to other approaches is the possibility of recovering the material and to use it again to treat more wastewater. The problem is that sometimes the catalysts are not stable enough to be reused, hindering the viability of implementing the treatment on a large scale. For this reason, assessing the reusability of the catalysts is important. Under the same operating conditions, the best catalyst was used in reutilization experiments. H_2O_2 and PCM concentrations in these tests are shown in Figure 5.

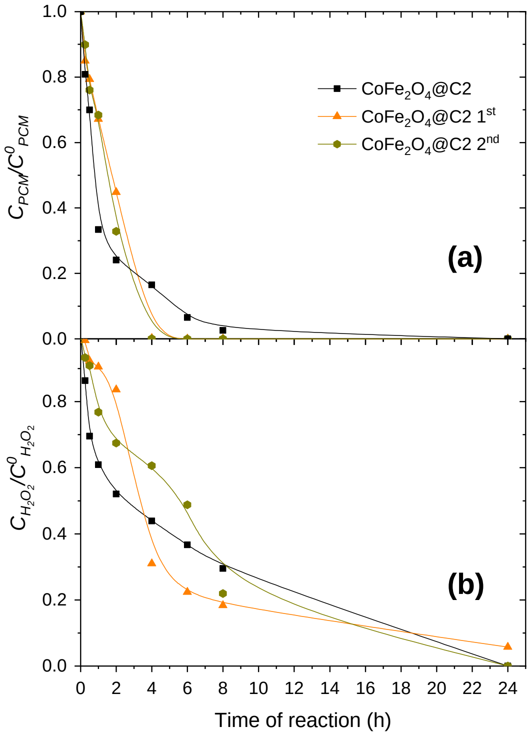

Figure 5. Normalized concentration of (a) PCM and (b) H_2O_2 in reutilization tests (lines connecting points are only indicating trends). Operating conditions: $C_{PCM,0}$ = 100 mg·L^{-1}, $C_{H_2O_2,0}$ = 472.4 mg·L^{-1}, C_{cat} = 2.5 g·L^{-1}, pH$_0$ = 3.5 and T = 80 °C.

The reutilization tests show that the catalytic activity of $CoFe_2O_4$@C2 slightly improved for PCM removal compared to the first run. This behavior can be related to changes in the surface chemistry of the catalyst by oxidation in the first contact with hydrogen peroxide, which changes its catalytic properties. The behavior is confirmed by the similar concentration profiles obtained when comparing 1st and 2nd runs.

4. Conclusion

In this work, the improved efficiency of carbon-coated MNPs on PCM removal by CWPO was shown. Characterization techniques showed the presence of carbon in the nanoparticle (FT-IR) and the increase in surface area due to the removal of silica. The evolution of PCM and H_2O_2 concentrations through time in the reaction runs showed that all nanomaterials have catalytic activity. Furthermore, pure adsorption tests showed that removals of PCM are negligible by this mechanism under the same opperating conditions than considered in CWPO. According to the results found in CWPO, the bare magnetic core is not recommended as a suitable catalyst since the decomposition of H_2O_2 and the removal of PCM were the lowest. Increased activity of both hybrid nanoparticles compared to bare core is related to the increase in surface area in coting, leading to an increase in the number of active sites and consequently increased catalytic efficiency In all results considered, $CoFe_2O_4$@C2 has shown the best performance, due to the more controlled H_2O_2 decomposition profile and lower adsorption. At last, the reutilization of $CoFe_2O_4$@C2 in CWPO showed a similar trend in the second and third repetitions, reinforcing the potential application of the catalyst for real scenarios. The results obtained here for this system are encouraging to test the material considering different organic pollutants.

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