

Magnetic Carbon Xerogels for the Catalytic Wet Peroxide Oxidation of 4-Nitrophenol Solutions

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1 Introduction

Catalytic wet peroxide oxidation (CWPO) is a well-known advanced oxidation process for the removal of organic pollutants from industrial process waters and wastewater. Specifically, CWPO employs hydrogen peroxide (H_2O_2) as oxidation source and a suitable catalyst to promote its decomposition via formation of hydroxyl radicals (HO^\bullet), which exhibit high oxidizing potential and serve as effective species in the destruction of a huge range of organic pollutants. When an iron salt is used in CWPO, through the so-called Fenton process, high degradation rates of organic pollutants are obtained. However, the Fenton process usually requires a final separation step for Fe ions present in the treated water, increasing the treatment costs. More recently, carbon materials have been shown as active metal-free catalysts for the CWPO of organic pollutants in aqueous solutions; nevertheless carbon materials still show low catalytic activity in comparison with metal-based catalysts.

In the present work, nanostructured hybrid composites containing iron magnetic species and carbon xerogels materials are synthesized and tested as catalysts in the CPWO of highly concentrated 4-nitrophenol solutions (5 g L^{-1}). In this way, the synergistic effects that can arise from the combination of the high catalytic activity of iron oxide species with the flexibility for tuning the textural properties of carbon-based materials are explored. In addition, *in-situ* magnetic separation of the catalysts at the end of the treatment process is a further advantage.

2 Materials and methods

A carbon xerogel (CX) was prepared by polycondensation of resorcinol with formaldehyde (with a molar ratio of 1:2), following the procedure described elsewhere: 9.91 g of resorcinol were dissolved in 18.8 mL of deionised water, 13.5 mL of formaldehyde solution being then added and the pH adjusted to 6.1. The gelation step was allowed to proceed at 85°C during 3 days, the recovered gel being afterwards grounded (particle sizes in the range 0.106-0.250 mm), dried in an oven (from 60°C to 150°C , defining a heating ramp of $20^\circ\text{C day}^{-1}$) and pyrolyzed at 800°C under a N_2 flow (100 mL min^{-1}) in a tubular vertical oven, resulting in CX materials. CX/ $\text{Fe}_{0.05}$ was synthesized using the same procedure, except that iron (III) chloride hexahydrate was added to the resorcinol solution (considering a Fe/resorcinol molar ratio of 0.05) prior to formaldehyde. The solids recovered from pyrolysis were then washed with 1 L of an HCl solution (pH = 3) at 50°C and dried overnight at 60°C , resulting in the CX/ $\text{Fe}_{0.05}$ materials.

CWPO experiments were conducted in a 250 mL well-stirred (600 rpm) glass reactor loaded with 50 mL of a 4-NP aqueous solution (5.0 g L^{-1}), during 24 h at $T = 50^\circ\text{C}$, considering a catalyst load = 2.5 g L^{-1} , and using the stoichiometric amount of H_2O_2 needed to completely

mineralize 4-NP (17.8 g L⁻¹). Pure adsorption runs and blank experiments, without catalyst, were also performed in order to discriminate the adsorption and non-catalytic components of 4-NP removal by CWPO, respectively.

3 Results and discussion

The ability of the magnetic composites to act as catalysts in the CWPO of 4-NP was evaluated. Comparisons between the removal of 4-NP by CWPO in the presence of CX and in a series of three consecutive runs using CX/Fe_{0.05} are shown in Figure 1a. Non-catalytic removal of 4-NP is also shown for comparison. As observed, a marked increase in the removal of 4-NP is observed when using CX/Fe_{0.05} as catalyst, even in its third consecutive reuse. In addition, adsorption of 4-NP on CX/Fe_{0.05} was found negligible (ca. 9%). Therefore, CX/Fe_{0.05} is univocally an active catalyst for CWPO of highly concentrated 4-NP solutions. Nevertheless, some Fe leaching was observed even at the end of the third run (4.8 mg L⁻¹). Bearing this in mind, the effect of the initial pH on the 4-NP removals and Fe leaching was assessed through an additional CWPO run performed without any pH adjustment. As observed in Figure 1b, the 4-NP removal decreased from 77% to 45% when the initial pH was not adjusted, whereas the Fe leaching dropped from 10.4 mg L⁻¹ (at pH = 3) to 2.5 mg L⁻¹. In this way, further studies are now being conducted in order to maximize catalyst activity and minimize Fe leaching levels, through the synthesis of magnetic carbon xerogels with improved Fe dispersion and stability.

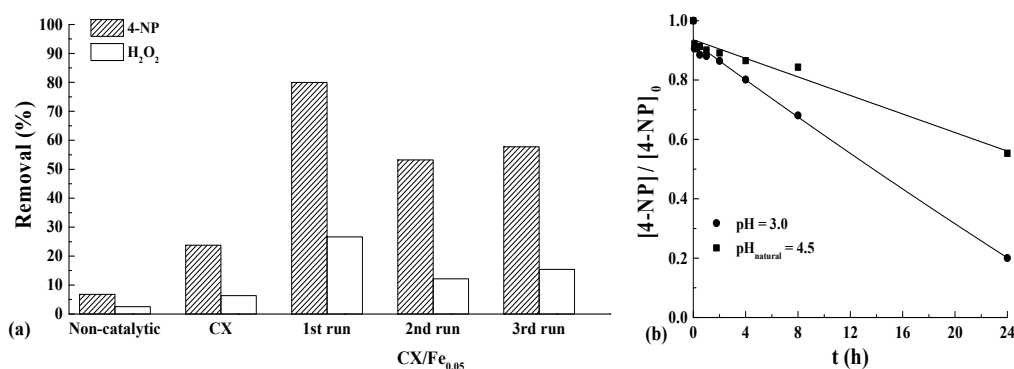


Fig. 1. (a) 4-NP and H₂O₂ removals obtained after 24 h in CWPO runs performed at pH = 3; (b) effect of the initial pH on the 4-NP removal by CWPO when using CX/Fe_{0.05} as catalyst.

4 Conclusions

High catalytic activity is obtained when magnetic carbon xerogels are used in the CWPO of highly concentrated 4-NP solutions. Nevertheless, further studies are required in order to increase the catalytic stability of these materials.

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