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Program and Abstracts

Organization
Core-shell nanocomposites prepared by hierarchical co-assembly: the role of the carbon shell in catalytic wet peroxide oxidation processes

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Magnetic nanomaterials have been finding interesting applications in various fields, such as information storage, refrigeration, biomedicine and catalysis. Regardless of their innovative aspects, these materials are prone to agglomerate and change their properties, due to their small size [1]. To avoid this situation, the nanoparticles can be strategically coated, leading to the development of core-shell nanocomposites. Among the coating materials available, carbon may be considered the best alternative, due to some of its specific properties, including: the high specific surface area; the possibility to control, to some extent, the porosity and surface chemistry; the stability in acidic/basic media; the structural stability at relatively high temperatures; and the unique electrical properties [1,2].

Core-shell nanostructures, with a magnetic core and a carbon shell, revealed already very promising in many different fields [1]. In particular, hybrid magnetic carbon nanocomposites were found to be promising catalysts for the catalytic wet peroxide oxidation (CWPO) – an advanced oxidation process based on the catalytic decomposition of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), leading to the formation of highly oxidative hydroxyl radicals (HO\textsuperscript{•}) [3]. In the present work, a hybrid magnetic graphitic nanocomposite (MGNC) was prepared by hierarchical co-assembly of magnetic nanoparticles (magnetite, Fe\textsubscript{3}O\textsubscript{4}) and carbon precursors, followed by thermal annealing. The advantages of using carbon encapsulated Fe\textsubscript{3}O\textsubscript{4} nanoparticles in CWPO processes were assessed using 4-nitrophenol (4-NP) as model refractory pollutant.

MGNC was synthesized by adapting the procedure described elsewhere [4]. Briefly, 5 g of copolymer pluronic F127 were dissolved in 50 mL of H\textsubscript{2}O. Then, 5 mL of Fe\textsubscript{3}O\textsubscript{4} suspension (17 mg mL\textsuperscript{–1}, previously obtained by co-precipitation of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} in basic solution, at 30 °C and under N\textsubscript{2} atmosphere) were added, the resulting solution being stirred during 2 h at 66 °C for homogenization. After that, ≈ 60 mL of phenol/formaldehyde resol solution were added, the resulting mixture being kept under stirring at 66 °C for 72 h and then at 70 °C for an additional 24 h. The recovered solids were washed with distilled water and then dried overnight at 60 °C. Afterwards, the sample was thermally annealed under N\textsubscript{2} flow (100 mL min\textsuperscript{–1}) at 800 °C. Finally, the sample was washed with 1 L of HCl solution (pH = 3) at 50 °C under vacuum filtration and dried overnight at 60 °C, resulting in the MGNC material.

Fig. 1. TEM micrographs of (a) Fe\textsubscript{3}O\textsubscript{4} and (b) MGNC.
The diffraction pattern of Fe$_3$O$_4$ (not shown) confirmed the presence of only one phase, corresponding to magnetite with a lattice parameter a = 8.357 Å and a crystallite size of 16.6 ± 0.2 nm. The diffraction pattern of MGNC (not shown) confirmed the presence of a graphitic phase, in addition to the metal phase, suggesting that Fe$_3$O$_4$ nanoparticles were successfully encapsulated within a graphitic structure during the synthesis of MGNC. The core-shell structure of MGNC is unequivocally demonstrated in the TEM micrograph shown in Fig. 2b. Characterization of the MGNC textural and surface chemical properties revealed: (i) stability up to 400 °C under oxidizing atmosphere; (ii) 27.3 wt.% of ashes (corresponding to the mass fraction of Fe$_3$O$_4$); (iii) a micro-mesoporous structure with a fairly well developed specific surface area ($S_{BET}$ = 330 m$^2$ g$^{-1}$); and (iv) neutral character (pH$_{PZC}$ = 7.1). In addition, the magnetic nature of MGNC (Fig. 2) is an additional advantage for possible implementation of in situ magnetic separation systems for catalyst recovery.

The performance of MGNC in the CWPO of 200 mg L$^{-1}$ 4-NP solutions was evaluated against that of bare Fe$_3$O$_4$. All the experiments were performed with a 4-NP/Fe$_3$O$_4$ mass ratio of 36.6, i.e. a 4-NP/MGNC mass ratio of 10 was used in the runs performed with the composite consisting of 27.3 wt.% of Fe$_3$O$_4$. As observed in Fig. 3, the catalytic activity is enhanced when the Fe$_3$O$_4$ magnetic material is encapsulated within a carbon shell in the MGNC catalyst. This behaviour may be explained by the presence of the carbon phase, which increases the adsorptive interactions between the surface of the catalyst and the pollutant molecules, attracting larger amounts of pollutant molecules to the vicinity of the active sites where highly oxidizing HO$^\bullet$ are generated, thus inhibiting non-efficient parasitic reactions involving H$_2$O$_2$ and HO$^\bullet$ [3]. At the same time, the confinement effect caused by the carbon shell protects the magnetic catalyst core, as shown by comparing the leaching of Fe species at the end of the CWPO experiments performed with Fe$_3$O$_4$ (0.98 mg L$^{-1}$) and MGNC (0.27 mg L$^{-1}$).

Thus, the beneficial effect of the carbon shell was highlighted, leading to unprecedented pollutant mass removals (5000 mg g$^{-1}$ h$^{-1}$) in CWPO, in particular when compared to other carbon-based [3] and magnetite-based [5] catalysts. Nevertheless, further catalyst optimization is envisaged in the follow up of this work.

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