Synthesis of hybrid magnetic carbon nanocomposites for catalytic wet peroxide oxidation

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Dissertation presented for the Ph.D. degree in the
Doctoral Program in Chemical and Biological Engineering at the Faculty of Engineering, University of Porto, Portugal

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ABSTRACT

Catalyst design plays a crucial role in catalytic wet peroxide oxidation (CWPO), since this water treatment technology relies on the catalytic decomposition of hydrogen peroxide (H_2O_2) via formation of hydroxyl radicals ($HO^{\bullet}$), which are very powerful and effective oxidants for the destruction of a huge range of recalcitrant organic pollutants. Several motivations have prompted the present Ph.D. studies on the synthesis and application of hybrid magnetic carbon nanocomposites in CWPO. Among these, a special focus was given to the synergies that can arise from the combination of highly active and magnetically separable iron species with the easily tuned properties of carbon-based materials. Bearing this in mind, the main objective of my studies was the synthesis of hybrid magnetic carbon nanocomposites with high activity and stability characteristics for the CWPO of organic pollutants typically untreatable by conventional biological means.

The first stage was devoted to the study of metal-free carbon materials. The results obtained highlighted the importance of the interplay between chemical and textural properties when developing efficient carbon-based catalysts for CWPO. Also of relevance were the adsorptive interactions between the pollutant molecules and the surface of the catalysts, when seeking for highly efficient CWPO applications.

Within the hybrid magnetic carbon composites, carbon structures decorated with magnetic particles were initially studied. For that purpose, magnetic carbon xerogels consisting of interconnected carbon microspheres with iron and/or cobalt microparticles embedded in their structure were prepared by inclusion of metal precursors during the sol-gel polymerization of resorcinol and formaldehyde, followed by thermal annealing. The results revealed a clear synergy arising from the simultaneous inclusion of iron and cobalt species within carbon frameworks, which was ascribed to (i) the enhanced accessibility to the active iron species at the surface of the catalyst promoted by the simultaneous incorporation of cobalt, (ii) the ability of metallic Co to catalyse H_2O_2 decomposition via $HO^{\bullet}$ radicals formation, and (iii) the efficient reduction of Fe^{3+} to Fe^{2+} promoted by metallic Co on the surface of the bimetallic catalyst.

Hybrid structures were considered afterwards in which the magnetic phase is protected against the environment by a carbonaceous shell. For that purpose, a hybrid magnetic graphitic nanocomposite, composed by a magnetite core and a graphitic shell, was synthesized by hierarchical co-assembly of magnetite nanoparticles and carbon precursors, followed by thermal annealing. It was found that the encapsulation of magnetite nanoparticles within carbon frameworks (iv) enhances the catalytic activity in CWPO when compared to bare magnetite, while (v) strongly limiting the leaching of iron species to the treated water.

A high-performance hybrid magnetic graphitic nanocomposite, composed by a cobalt ferrite core and a graphitic shell ($CoFe_2O_4$/MGNC), was then prepared based on the findings previously obtained. The positive effects described in (ii) to (iv) were in this way potentially combined in the same nanocomposite. The application of this new generation catalyst enabled the treatment of a liquid effluent from a mechanical biological treatment plant for municipal solid waste, regardless of its very high pollutant load. In addition, a magnetic separation system was developed for the *in-situ* recovery of $CoFe_2O_4$/MGNC after the CWPO reaction stage. This approach allowed demonstrating the high stability of $CoFe_2O_4$/MGNC for CWPO, through a series of five CWPO reaction/magnetic separation sequential experiments performed in the same vessel.

Although the works reported followed a current trend towards the application of CWPO under intensified conditions (i.e., with higher pollutant concentrations and lower catalyst loads), the ability of this water treatment technology for the elimination of contaminants of emerging concern was also evaluated. Specifically, the ability of CWPO for the degradation of the antimicrobial agent sulfamethoxazole in secondary treated wastewater was shown in a case-study performed during a short-term scientific mission for advanced training at the University of Patras, Greece, under the framework of COST Action ES1403: NEREUS.

Summarizing, the knowledge on the surface reactions and interactions involved when CWPO is carried out in the presence of hybrid magnetic carbon nanocomposites, is the main contribution of my Ph.D. dissertation. This knowledge is fundamental for the design of materials with potential effectiveness for real-scale applications.