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Review

Catalytic wet peroxide oxidation: a route towards the application of hybrid magnetic carbon nanocomposites for the degradation of organic pollutants. A review

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ABSTRACT

Several motivations have prompted the scientific community towards the application of hybrid magnetic carbon nanocomposites in catalytic wet peroxide oxidation (CWPO) processes. The most relevant literature on this topic is reviewed, with a special focus on 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. These are mainly ascribed to increased adsorptive interactions, to good structural stability and low leaching levels of the metal species, and to increased regeneration and dispersion of the active sites, which are promoted by the presence of the carbon-based materials in the composites.

The most significant features of carbon materials that may be further explored in the design of improved hybrid magnetic catalysts are also addressed, taking into consideration the experimental knowledge gathered by the authors in their studies and development of carbon-based catalysts for CWPO. The presence of stable metal impurities, basic active sites and sulphur-containing functionalities, as well as high specific surface area, adequate porous texture, adsorptive interactions and structural defects, are shown to increase the activity of carbon materials when applied in CWPO, while the presence of acidic oxygen-containing functionalities has the opposite effect.

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1. Introduction

With the increasing scarcity of clean water sources, wastewater treatment, and even reuse, became of utmost importance. Therefore, the development of efficient and economically viable technologies, able to meet increasingly demanding quality criteria for sustainable and safe urban water cycles and the use of treated wastewater as a reliable alternative water source, is presently of high priority in the policy agendas of European Union (EU) member states and many other countries around the world [1]. Therefore, the development of efficient technologies capable of degrading toxic, persistent and bio-recalcitrant organic pollutants commonly associated with negative impacts on conventional biological wastewater treatment processes, such as endocrine disrupting compounds, many types of pharmaceutical drugs including antibiotics, disinfection by-products, personal care products, metabolites, transformation products, pesticides, surfactants and biocides, has received a great deal of attention from the scientific community, in particular the so called Advanced Oxidation Processes (AOP) [1].

Among the AOP, catalytic wet peroxide oxidation (CWPO) is recognized as a low cost technology [2], since it operates with simple equipment and under mild conditions (e.g., at atmospheric pressure and low temperatures) [3]. CWPO employs hydrogen peroxide (H_2O_2) as oxidation source and a suitable catalyst to promote its partial decomposition to hydroxyl radicals ($HO^•$), highly oxidizing species able to efficiently degrade most of the organic pollutants present in wastewaters [4,5]. Moreover, H_2O_2 is well-established as an environmentally-friendly agent, since its total decomposition products are oxygen and water, rendering CWPO-based water treatment technologies further attractive from an environmental point of view [3].

However, further optimization of catalyst design is still required in order to bring CWPO to the forefront of the most efficient AOP technologies. Bearing this in mind, the bibliometric analysis in Fig. 1 and the expertise gathered by the authors in their studies on carbon-based catalysts for CWPO prompted the preparation of this review on the synthesis of nanostructured hybrid magnetic carbon materials for CWPO applications. The background, main developments, and mechanistic aspects of the CWPO process, specially related with the application of carbon-based catalysts, are presented initially. Thereafter, the most significant results and conclusions reported in publications dealing with hybrid magnetic carbon catalysts for the degradation of organic pollutants by CWPO are thoroughly analysed and discussed. Since carbon materials present very specific features that may open prospects for the optimization of hybrid magnetic carbon materials for CWPO applications, the most significant results reported on the influence of carbon material properties on the efficiency of CWPO processes are also discussed in detail. In addition, all the pollutants used in the works reported in the literature on the application of carbon-based catalysts in CWPO processes are listed in Table 1.

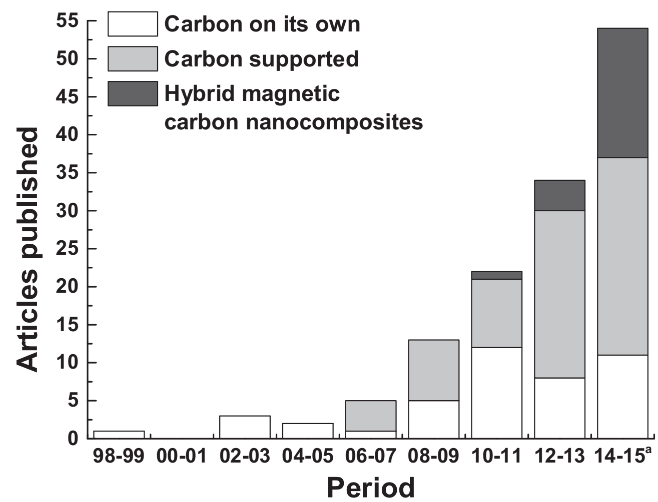

Fig. 1. Evolution of Scopus indexed original research articles dealing with the application of carbon-based materials in CWPO processes.
[a]Data collected from Scopus in November, 2015.

2. Catalytic wet peroxide oxidation: background, motivations and mechanistic aspects

2.1. The Fenton process

The catalytic oxidation of organic compounds using H_2O_2 as oxidant was first reported in the late XIX century, when the British researcher Henry John H. Fenton published his work on the oxidation of tartaric acid in the presence of iron salts [133]. In that work, it was demonstrated that tartaric acid can be oxidized by the interaction of small amounts of ferrous ion (Fe^{2+}) with distinct oxidizing agents, H_2O_2 leading to the best results. Fenton concluded that Fe^{2+} takes part in the reaction as catalyst, with a very small amount being enough to promote the complete degradation of an almost unlimited quantity of tartaric acid without being consumed.

In the 1930s, Fritz Haber and Joseph J. Weiss brought further insights on the phenomenon reported by Fenton, concluding that hydroxyl radicals ($HO^•$) – generated from the reaction of H_2O_2 with the superoxide radical anion ($O_2^{•-}$), the Haber-Weiss reaction [134] – were actually the active species responsible for the oxidation of tartaric acid, and not H_2O_2 itself. According to these authors, the interaction between H_2O_2 and Fe^{2+} in acidic media results in the decomposition of H_2O_2 through the oxidation of Fe^{2+} to ferric ion (Fe^{3+}), with the formation of hydroxide ions (OH^-) and $HO^•$ radicals, as described by Eq. (1) [135].

$$H_2O_2 + Fe^{2+} \rightleftarrows OH^- + HO^• + Fe^{3+} \quad (1)$$

The participation of Fe^{2+} as catalyst in the oxidation process was finally demonstrated in the 1950s, in two works reported by Barb et al. [136,137]. These authors proposed a two-step mechanism in