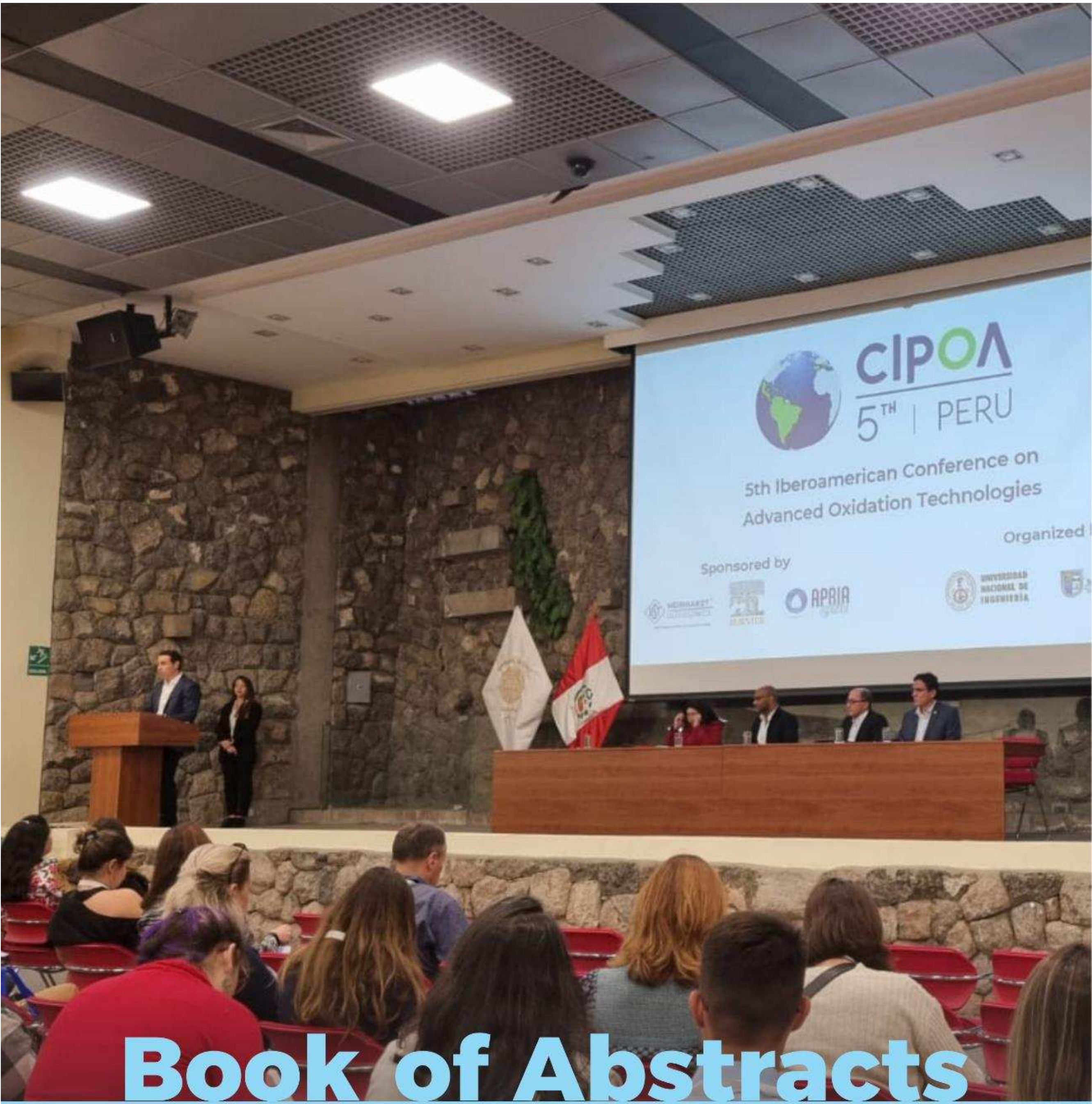

Book of Abstracts

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Wet peroxide oxidation of paracetamol using carbon-coated spinel ferrite nanoparticles as catalyst

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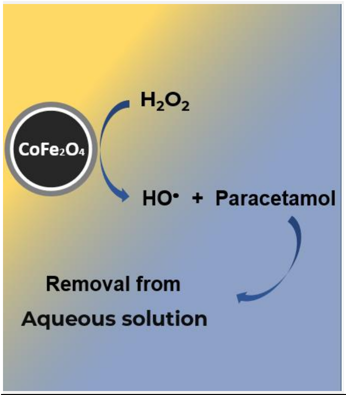

In this study, carbon-based magnetic nanoparticles (MNPs) have been prepared by sucessive sol-gel method for core bare preparation and carbon coated through polymerization of phloroglucinol/glyoxylic acid, which are greener carbon precursors than the conventional method of resorcinol/formaldehyde (R/F), since formaldehyde is known to be a carcinogenic reagent.

The bare core ($CoFe_2O_4$) and the carbon-coated MNPs ($CoFe_2O_4$@C) were tested as catalysts in the removal of paracetamol (PCM) from an aqueous solution by catalytic wet peroxide oxidation under optimum operational conditions, pH 3.5 and 80 °C. Values of paracetamol abatment between 33.0 and 100% were achieved after 6 h of reaction for the bare core and the carbon-based MNPs, respectively.

Introduction

Pharmaceutical compounds have become environmental pollutants of emerging concern, due to their intrinsic biological activity, which may cause adverse effects on aquatic and terrestrial ecosystems [1]. Acetaminophen, also known as paracetamol (PCM), represents one of the most used pharmaceutical compounds worldwide for analgesic and antipyretic use.

Several studies have reported the presence of paracetamol in surface waters, groundwaters and drinking waters [1]. The occurrence of this compound in aquatic environments is related to the inefficiency of its removal by conventional treatments provided by wastewater treatment plants and, as a result, it is discharged into the receiving streams.

In this context, catalytic wet peroxide oxidation (CWPO) has shown promising results for removing pharmaceutical compounds from aquatic environments [2,3]. Usually, this process consists on the use of an iron-based catalyst and hydrogen peroxide (H_2O_2) as oxidant. The catalyst decomposes hydrogen peroxide into hydroxyl radicals (HO•), leading to the degradation of non-biodegradable substances due to its high oxidation power [3].

However, due to the narrow working pH range, some problems may be associated with the use of metal-based catalysts, such as iron leaching and catalyst aggregation. As a way of overcoming these disadvantages, carbon coating of metal nanoparticles is a strategy to protect them from physicochemical changes, improving its catalytic activity and stability [2].

Therefore, the aim of the present work is to investigate the degradation of PCM in a CWPO process using two types of catalysts. A bare core ($CoFe_2O_4$) and a novel catalyst comprised of a carbon-coated magnetic ferrite ($CoFe_2O_4$@C).

Material and Methods

Carbon-coated magnetic nanoparticles (MNPs) were prepared by adapting the methodology described in previous works [4]. In brief, the core of spinel ferrite ($CoFe_2O_4$) nanostructures was synthesized through a sol-gel method and the coating was obtained using phloroglucinol/glyoxylic acid as precursors of the carbon layer.

Oxidation runs were performed with a PCM concentration of 100 ppm, the stoichiometric amount of H_2O_2 needed to mineralize completely PCM, initial pH 3.5, catalyst dosage of 2.5 $g \cdot L^{-1}$, and temperature of 80 °C. Non-catalytic and adsorption runs were done under the same operating conditions in the absence of catalyst and H_2O_2, respectively. PCM and H_2O_2 concentrations were followed against reaction time using the methods described in a previous work [2].

Results and Discussion

The evolution of the relative concentration of PCM and H_2O_2 throughout the reaction is represented in Figure 1. Without a catalyst, H_2O_2 was not significantly decomposed and after 24 h of reaction time, no significant values of pollutant removal were noted.

By analysis of Figure 1 (b), different H_2O_2 decomposition profiles are observed. After 4 h of reaction, 30.4% and 56.1% of the initial concentration of H_2O_2 were decomposed by $CoFe_2O_4$ and $CoFe_2O_4$@C, respectively.

The increase of 25.7% in H_2O_2 decomposition presented by the $CoFe_2O_4$@C nanoparticles when comparing with $CoFe_2O_4$ can be related to the synergistic effect between a metal-based core and carbon shell, in which these structures are known to have activity in the decomposition of H_2O_2 into hydroxyl radicals.

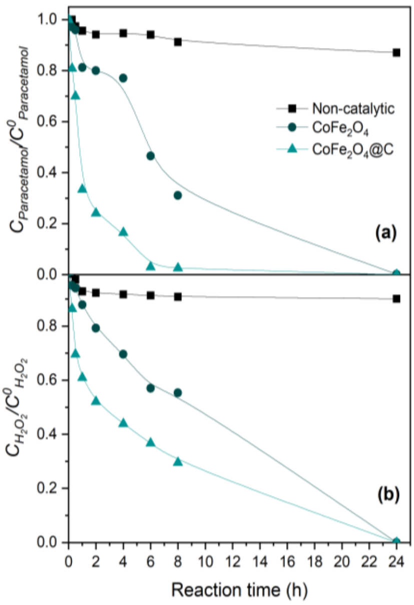

Figure 1 – Concentration of (a) paracetamol, and (b) H_2O_2 throughout oxidation reactions. Lines are only used to guide reading the removal trends.

It is well-know that the degradation of organic pollutants depends on the quantity of hydroxyl radicals formed during the decomposition of H_2O_2. Thus, the amount of generated $HO^•$ radicals is a crucial parameter for understanding the degradation of PCM. As can be seen in Figure 1 (a), coating the magnetic core with a carbon layer led to increased hydrogen peroxide decomposition, which consequently led to an increase in paracetamol removal from 33.0% for the bare core to 83.5% for the carbon-based nanoparticles, representing an increase of 50.5% in the removal of the pollutant. Moreover, after 6 h of reaction time, PCM was fully converted when using the carbon-based MNPs as catalyst, while for the bare core, only 54% of removal was observed for the same period.

This result shows that the catalytic activity is enhanced when $CoFe_2O_4$ is encapsulated with a carbon shell. The increase in paracetamol removal from the matrix might be related to the increase of adsorptive interactions between the surface area of the catalyst and the molecule of the pollutant, attracting a higher quantity of molecules to the surroundings of the active sites, where highly oxidizing radicals are formed, leading to the higher removal of PCM [4].

Adsorption experiments in the absence of H_2O_2 were performed to verify if the pollutant is mainly removed via the oxidation process or if the pollutant is being adsorbed on the catalyst surface. PCM removal reached values of 4.5 and 7.1% after 6 h of contact time for $CoFe_2O_4$ and $CoFe_2O_4@C$, respectively. Whereas in CWPO runs at the same time of reaction a fully removal of PCM was obtained for the carbon-based MNPs and 54.0% for the bare core. Thus, the results show that PCM is being removed mainly through oxidation, in which adsorption presents a low contribution in its removal.

Conclusions and future work

CWPO paracetamol was successfully performed using two types of iron-based nanoparticles to assess the performance enhancement of a carbon shell layer covering a magnetic core. Complete conversion of paracetamol was achieved within 6 h of reaction using the carbon-based nanoparticles as catalyst. The enhanced performance of catalytic activity is related to the increase of adsorptive interactions between the surface of the catalyst, the hydroxyl radicals and PCM. In addition, it was found that PCM is removed mainly via CWPO, in which the adsorption presents a low contribution for the pollutant removal. Therefore, the carbon-coated catalyst used in this work shows promising results for the removal of organic pollutants from wastewater. In future, a deep study related to the chemistry surface and stability of $CoFe_2O_4@C$ will be performed to elucidate the increased catalytic activity of the carbon-coated catalyst compared to the core bare.

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