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On behalf of the Organizing and Scientific Committees, we extend a warm welcome to the 6th Iberoamerican Conference on Advanced Oxidation Technologies (VI CIPOA), taking place in Florianópolis, Brazil, from October 7th to 11th, 2024.

The CIPOA conference aims to bring together scientists, Ph.D. students, master's and undergraduate students, and professionals to share their research findings and engage in discussions about the future directions and opportunities in Advanced Oxidation Technologies. The focus areas encompass environmental protection, chemical and food engineering, energy, and climate sectors, all contributing to a sustainable and carbon-neutral circular economy.

The conference program will encompass a diverse range of engaging sessions, including invited lectures, oral communications, short oral communications for Ph.D. students, poster communications, and an interactive round-table discussion.

We cordially invite you to submit your abstracts for poster or oral presentations to the 6th Iberoamerican Conference on Advanced Oxidation Technologies. We eagerly await your contributions to the scientific program and sincerely appreciate your support in advance!

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(Chairwoman VI CIPOA 2024)

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Fe₃O₄@ZIF67-based metal-organic framework as heterogeneous catalyst for Brilliant Green dye removal in aqueous matrices by photo-Fenton process

SHORT-ORAL +
POSTER

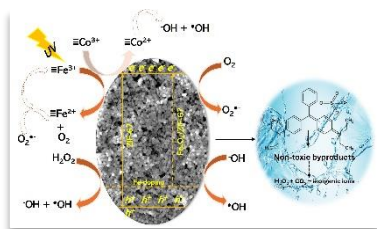
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Brilliant Green (BG) is a organic dye characterized by its toxicity to biota and aquatic organisms. In this work, structure of Fe₃O₄@ZIF67 cobined with UV radiation was applied as heterogeneous catalyst in the BG removal by photo-Fenton process. The tests were performed by analyzing the influence of the pH, catalyst mass and volume of H₂O₂. By optimization parameters (pH 4.7, V_{H₂O₂}= 50 µL, m_{catalyst}= 2.5 mg and, [BG]=5.0 mg L⁻¹) the photo-Fenton process was applied in the aqueous matrices (tap water, river water, well water and sea water). In all cases, 100% elimination of the BG dye was reached, and the and the maximum of TOC removal was 85%, after 30 min. Treatment of BG dye by photo-Fenton process resulted in low-toxicity byproducts, as confirmed by the *Lactuca sativa* L. method. The Fe₃O₄@ZIF67 structure exhibited excellent catalytic stability, maintaining their activity after nine consecutive degradation cycles. No significant changes were observed in the FTIR spectra and XRD patterns of the catalysts after use.

Introduction

Water pollution poses a significant environmental challenge in the face of rapid industrial and economic progress. Organic pollutants, including chemical dyes, are prevalent in various water bodies. Most of these pollutants exhibit high stability and low biodegradability, leading to detrimental effects on the health of living organisms. Consequently, technologies that enable efficient removal of these compounds have emerged as promising remediation alternatives for diverse types of effluents [1]. AOPs have emerged as effective wastewater treatment technologies due to their ability to generate highly oxidizing species using irradiated energy and/or catalysts [2]. In this context, the development of efficient visible light photocatalysts is particularly relevant, as it exhibit remarkable catalytic performance, especially when combined with the Fenton process. Zeolitic imidazolate frameworks (ZIFs), a type of metal-organic framework (MOF), have garnered increasing interest due to their unique properties and ease of forming composites with iron nanoparticles [3]. Among these, ZIF-67(Co) and ZIF-8(Zn) stand out as photocatalysts in organic compound degradation processes. These structures can be combined with other materials, such as semiconductors and metal oxides, to enhance their morphology and photoactivity. This leads to the formation of active sites that promote greater functionality of the ZIF crystal structure in a single material, making them potentially superior to pure ZIFs [4]. Considering the catalytic coupling between ZIFs and iron nanoparticles, this study focuses on

the synthesis of magnetic Fe₃O₄@ZIF-67 structure and it application as heterogeneous catalyst in the photo-Fenton process for BG dye degradation.

Material and Methods

For the synthesis of Fe₃O₄-based ZIF67 structures, the following mass-to-mass (m/m) ratios of the magnetic material were established: 2.0, 4.0, 6.0, and 8.0%. The precursor solution of the organic ligand (2-methylimidazole) and the metal ion (Co) was prepared separately in 50 mL of methanol. These solutions were mixed and added to the Fe₃O₄ NPs in the respective compositions, and the reaction proceeded for 24h under constant stirring. Subsequently, the samples were washed with ethanol and dried at 60 °C for 12h. The ZIF structures were characterized by XRD, SEM-FEG, FTIR, pHPCZ, band-gap analysis, photocurrent study and EIS. The photocurrent study (in the presence of UV radiation) and EIS were carried out on a GC electrode in the presence of 0.05 mol L⁻¹ K₂SO₄ at pH 4.7, and conducted in a potentiostat/galvanostat (Metrohm/Autolab). For the degradation experiments, 50 mL of a BG aqueous solution (pH 2.5, 4.7 and 10), was placed in a flow-by reactor, assisted by a light source (UVC lamp, Hg 125W). The dye removal rate was followed by the absorbance decay monitored by UV-Vis spectrometry. For toxicity evaluation, the experiments were conducted using seeds of *Lactuca sativa* L. Experiments were carried out to verify the influence of the analysis of active radical species O₂^{•-}, h⁺, •OH and e⁻ during the degradation process.

Quantification tests for inorganic ions were also carried out in real aquatic matrices using ion chromatography (Metrohm CH-9101 Herisau Ionic Chromatograph).

Results and Discussion

Characterization of Fe₃O₄@ZIF-67 structures

Fig. 1a and 1b shows the XRD patterns and band-gap analysis, respectively, to modified ZIF-67 structure with magnetic NPs. The most prominent diffraction peaks for ZIF-67 were observed at 7.23, 10.28, 12.65, 14.61, 16.38 and 17.98°, confirming the formation of its pure phase. In the Fe₃O₄@ZIF-67 structures, the corresponding crystal planes were also observed, confirming that the presence of Fe₃O₄ NPs did not cause any structural changes. This indicates that all phases are compatible with the sodalite crystal structure. Diffuse reflectance spectroscopy analysis revealed bands characteristic of *d-d* ligand field transitions for Co²⁺. These bands are associated with the metal-ligand coordination, specifically the ⁴A₂(F) → ⁴T₁(P) transition between Co²⁺ and N atom (ligand) in tetrahedral sites, exhibiting spin-coupled triplet character. The E_{g1} value, corresponding to the visible region absorption, was 1.96 eV. In the UV region, E_{g2} and E_{g3} values ranged between 3.44 and 3.67 eV. The energy values indicate the materials' potential for visible light excitation, enabling the generation of (e⁻/h⁺) pairs and promoting photocatalytic activity.

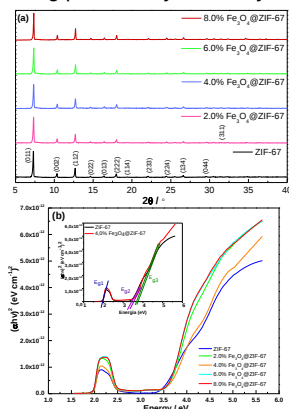


Figure 1. (a) XRD patterns and (b) Tauc graphic of the Fe₃O₄@ZIF-67 structures

BG degradation under photo-Fenton-based process

Fig. 2a illustrates that ZIF-67 achieves the highest color removal (65%) through photocatalysis. This enhanced performance is likely due to the generation of electron-hole (e⁻/h⁺) pairs on the material's surface upon irradiation activation. For comparison, the photolysis process and H₂O₂ addition alone yielded a maximum color removal of approximately 43%. The high adsorption capacity (65-73%) observed for ZIF-67 contributes significantly to BG removal. This is because the catalyst surface

possesses positive charges at a solution pH (4.7) below the pH_{pzc} (point of zero charge). Additionally, the porous textural characteristics of these materials further enhance their efficiency. Fig. 2b suggests that the 2.0% Fe₃O₄@ZIF-67 catalyst exhibits a higher color removal tendency (~67%). While other compositions achieve similar results at the final reaction time, the 2.0% Fe₃O₄ loading offers a potential advantage. This enhanced performance can be attributed to the ability of Fe²⁺ ions on the Fe₃O₄ NPs to act as electron donors. Notably, the octahedral sites within the Fe₃O₄ crystal structure can accommodate both Fe²⁺ and Fe³⁺ ions, facilitating the reversible oxidation of Fe²⁺ ions. Fig. 2c demonstrates the behavior of catalysts in the face of pH variation in photo-Fenton degradation. It is noted that all compositions are efficient catalytic materials applied to the degradation of BG dye at pH 4.7, achieving ~100% removal.

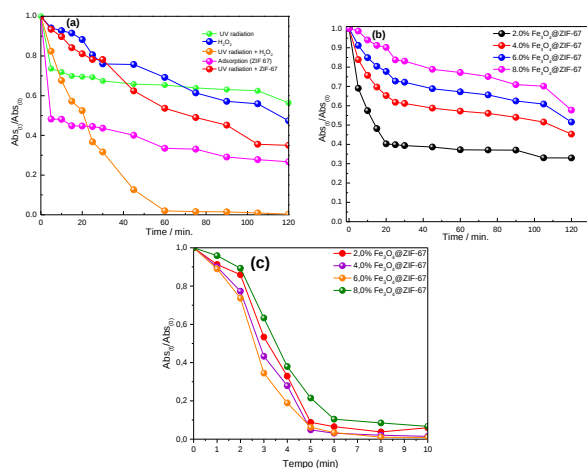


Figure 2. Absorbance decay of BG dye degradation at pH 4.7 by (a) ZIF-67 as catalyst and Fe₃O₄@ZIF-67 applied in the (b) photocatalytic and (c) photo-Fenton process.

Data revealed that the presence of various scavengers affects the degradation rate of the dye in the photo-Fenton process using the 4.0% Fe₃O₄@ZIF-67. Compared to the control experiment (without scavengers, ~100% degradation), the degradation rate decreased to 86.3, 29.7, 82.5, and 73.3% in the presence of isopropyl alcohol, benzoquinone, sodium oxalate, and silver nitrate, respectively. This significant decrease, particularly with benzoquinone (~70% reduction), suggests that O₂^{•-} plays a dominant role in dye degradation.

BG degradation in aqueous matrices under photo-Fenton-based process

In this stage, the degradation of 5.0 mg L⁻¹ BG in tap water, river water, well water and sea water samples was evaluated by using 4.0% Fe₃O₄@ZIF-67 as catalyst in the photo-Fenton process at pH 4.7. The results indicate a slight decrease in dye removal efficiency compared to experiments using deionized

water, particularly in well water and tap water. This decrease can likely be attributed to the presence of inorganic species, such as $\text{CO}_3^{2-}/\text{HCO}_3^-$, which can hinder the formation of active radicals necessary for dye removal. Additionally, organic matter naturally present in some water sources, especially river water, might also contribute to the decrease in

efficiency. Furthermore, dye removal efficiency in seawater is also reduced. This can be explained by the formation of stable complexes between the dye molecules and seawater components. These complexes are difficult to degrade through the chosen method.

Conclusion

Our study successfully employed $\text{Fe}_3\text{O}_4@\text{ZIF-67}$ composites in various proportions as heterogeneous catalysts for the photocatalytic degradation of GB dye combined with the Fenton process. The catalysts exhibited unique structural and compositional properties, leading to excellent light absorption, efficient charge transfer, and rapid regeneration of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ redox couples, ultimately promoting the generation of free radicals. We also identified $\text{O}_2^{\cdot-}$ as the primary species responsible for dye degradation. Interestingly, when evaluating degradation in different water matrices, minimal interference from inorganic and organic matter on GB removal efficiency was observed. However, subsequent experiments revealed that specific inorganic ions, namely CO_3^{2-} , SO_4^{2-} , Cl^- , and PO_4^{3-} can hinder the degradation efficiency rate.

Acknowledgments

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