

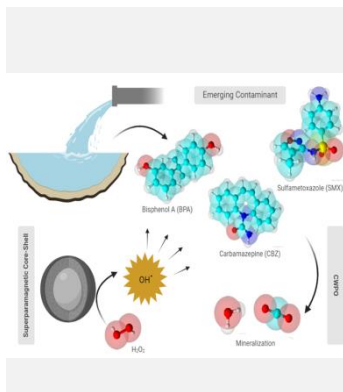
Superparamagnetic Core-Shell Nanoparticles for Removal of Emerging Contaminants by CWPO

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Water polluted with emerging contaminants significantly threatens environmental and human health. Conventional water treatment methods often fail to remove these contaminants efficiently. Catalytic wet peroxide oxidation (CWPO) emerges as a promising technique for the degradation of various organic micropollutants. This study presents the application of superparamagnetic core-shell nanoparticles to remove the emerging contaminants bisphenol A, carbamazepine and sulfamethoxazole by CWPO in single and multicomponent aqueous matrices. A superparamagnetic magnetite core (Fe_3O_4) was synthesized via solution combustion synthesis (SCS), and a carbon shell coating was deposited by an innovative green route considering phloroglucinol and glyoxalic acid ($\text{Fe}_3\text{O}_4@\text{C}$). The results highlight the efficiency of superparamagnetic nanocatalysts $\text{Fe}_3\text{O}_4@\text{C}$ in the removal of emerging contaminants from water by CWPO.

Introduction

Water pollution caused by emerging contaminants (ECs), such as pharmaceuticals, personal care products, pesticides, and industrial chemicals, is a global concern due to its adverse effects on aquatic ecosystems and human health, even at trace concentrations [1]. Due to its recalcitrant nature, conventional water treatment methods are ineffective in completely removing ECs, leading to a critical need for advanced treatment techniques capable to degrade efficiently emerging contaminants in water. This problematic was highlighted by the European Commission, which proposed the Urban Wastewater Treatment Directive, suggesting the application of quaternary treatments to ensure the removal of ECs from urban wastewater [2]. Catalytic Wet Peroxide Oxidation (CWPO) has emerged as a promising method for the degradation of organic pollutants in water by use of a solid catalyst in the presence of hydrogen peroxide (H_2O_2) to generate hydroxyl radicals (HO^\bullet), which effectively degrade a wide range of organic compounds [1]. The efficiency of CWPO depends on the catalyst's activity, stability, and recyclability. Superparamagnetic core-shell nanoparticles, consisting of a magnetic core (e.g., iron oxide) coated with a catalytically active shell (e.g., carbon-based materials), offer a promising solution for water treatment. The magnetic core facilitates easy separation of the nanoparticles from treated water using an external magnetic field, while the catalytic shell aids in degrading contaminants during CWPO. This study aimed to utilize superparamagnetic core-shell $\text{Fe}_3\text{O}_4@\text{C}$

nanoparticles in CWPO to remove the ECs bisphenol A (BPA), carbamazepine (CBZ), and sulfamethoxazole (SMX) in single and multicomponent aqueous matrices.

Material and Methods

The superparamagnetic magnetite core (Fe_3O_4) was synthesized by solution combustion synthesis (SCS) with 12 mM citric acid solution and 21 mM iron (III) nitrate solution, which was heated at 80°C in oven for 6.5 h until a brownish gel is formed. Next, the gel is subjected to 1 h N_2 purge followed by the combustion step. For the combustion, the gel was placed in an oil bath with stirring at 180°C for 3 h, also in an N_2 atmosphere. The material was washed with distilled water and absolute ethanol until neutral pH, and dried overnight in oven at 60°C . Subsequently, the magnetite core was coated by an innovative green route considering phloroglucinol and glyoxalic acid as carbon precursors. This method involved suspending 0.25 g of core in 50 mL of distilled water with ultrasound, then transferring it to a flask with ammonia solution and 0.1 g of phloroglucinol and Pluronic[®] F-127. After stirring for 1 h at 30°C , TEOS and glyoxalic acid were added, and the reaction proceeded for 6 h at the same temperature. The temperature was raised to 80°C for 8 h. The material was recovered, washed with water and absolute ethanol until neutral pH, and separated using a magnet. The resulting nanoparticles ($\text{Fe}_3\text{O}_4@\text{SiO}_2\cdot\text{C}$) were etched in 10 M NaOH solution for 16 h at room temperature to remove silica, and washed until neutral pH with water and

absolute ethanol, obtaining $\text{Fe}_3\text{O}_4@\text{C}$. CWPO experiments were conducted in a batch reactor system with magnetic stirring for single and multicomponent aqueous matrices using 50 mL of emerging contaminant: BPA, CBZ, SMX, and MIX (mixture of all ECs) at 10 ppm concentration and pH at 3.5. Systems without catalysts, with magnetite (Fe_3O_4) and superparamagnetic core-shell ($\text{Fe}_3\text{O}_4@\text{C}$) were evaluated at 2.5 g L^{-1} concentration and stoichiometric amount of H_2O_2 for the complete oxidation. The reaction was maintained at 80°C for 8 h and aliquots were withdrawn at regular intervals (0, 15, 30, 60, 120, 240, 360, and 480 min). The contaminant concentrations were analyzed using HPLC-UV/Vis at 280 nm and H_2O_2 concentration in a spectrophotometer (PG instruments) at 405 nm.

Results and Discussion

The catalytic activity of superparamagnetic nanoparticles was evaluated through CWPO experiments, after 480 min of reaction, using the ECs as model compounds. Figure 1 illustrates the percentage of removal of ECs after CWPO treatment for single (BPA, CBZ, SMX) and multicomponent (MIX) aqueous matrices obtained without catalyst and using Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{C}$ nanocatalysts. The non-catalytic run achieved 38, 28, 29, and 16% of BPA, CBZ, SMX and MIX removal, respectively. In the absence of catalyst, a low contaminant removal was observed, indicating a small contribution from the non-catalytic process to the degradation of the compounds. For the CWPO reaction using Fe_3O_4 , notable reductions in contaminant concentration were achieved, with removal percentages of 80, 66, 70, and 85% for BPA, CBZ, SMX and MIX respectively. This increase in removal efficiency suggests a strong interaction between contaminants and Fe_3O_4 nanoparticles, promoting rapid oxidation of the target compounds. Furthermore, the incorporation of carbon ($\text{Fe}_3\text{O}_4@\text{C}$) into the nanoparticle structure showed even more significant performance, with removal percentages of 91, 92, 90 and, 96% for BPA, CBZ, SMX and MIX, respectively. This

Conclusions

The results highlight the efficiency of the superparamagnetic nanoparticles Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{C}$, as catalysts in the removal of emerging contaminants from water by CWPO. These nanocatalysts resulted in a notable improvement in contaminant removal efficiency, for individual compounds and multicomponent mixture. The analysis also showed that the incorporation of carbon into the nanoparticle structure promoted an additional increase in the removal efficiency. These results have significant implications for the development of more efficient water treatment technologies, promising a solution to treat water polluted with emerging contaminants.

Acknowledgments

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References

- [1] A. S. Silva, F. F. Roman, A. V. Dias, J. L. Diaz deTuesta, A. Narcizo, A. P. F. da Silva, I. Çaha, F. L. Deepak, M. Bañobre-López, A. M. C. Ferrari, H. T. Gomes. *Journal of Environmental Chemical Engineering*, 11 (2023) 110806.
- [2] European Commission, *Directive of the European Parliament and of the Council concerning urban wastewater treatment (recast)*, 2022.

suggests that the presence of carbon on the surface of Fe_3O_4 nanoparticles can increase catalytic activity, possibly providing additional sites for the surface adsorption and oxidation of contaminants.

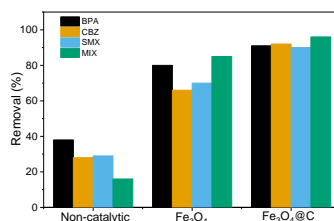


Figure 1. Contaminant removal (%) after CWPO treatment for single and multicomponent aqueous matrices.

Figure 2 presents the degradation of H_2O_2 during the CWPO process for the different studied systems. It was observed that the presence of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{C}$ nanocatalysts significantly increased the decomposition of hydrogen peroxide, indicating a greater production of hydroxyl radicals, responsible for the degradation of contaminants, promoting greater catalytic activity of nanomaterials.

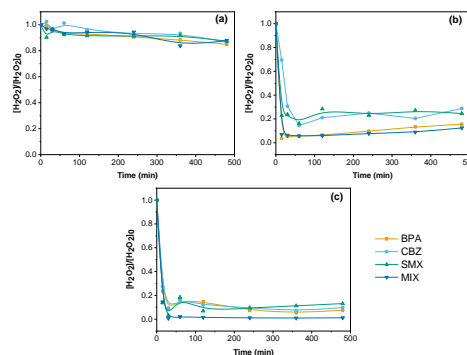


Figure 2. H_2O_2 degradation during CWPO reactions for the different studied systems: (a) without catalyst; (b) with Fe_3O_4 and (c) with $\text{Fe}_3\text{O}_4@\text{C}$.