Manganese ferrite and reduced graphene oxide photocatalyst supported on bone char for hydroxychloroquine removal

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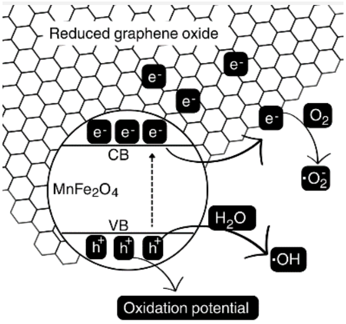

Hydroxychloroquine is a drug that is part of the class of emerging persistent contaminants. Studies aimed at removing this type of contaminant from water are necessary, as its presence can cause some adverse effects on human health and the ecosystem. Therefore, a heterostructured photocatalyst of manganese ferrite, reduced graphene oxide (G) supported on bovine bone char was synthesized to remove hydroxychloroquine from water through the heterogeneous photocatalysis process. The objective of this research was to evaluate the influence of the amount of G in the photocatalyst, and its contribution to the efficiency of the photocatalytic process. The photocatalyst with the greater mass of G, denominated CP-GM20, presented better photocatalytic performance than the others, demonstrating that G has the ability to contribute to improving the material photocatalytic performance.

Introduction

Emerging persistent contaminants are considered potentially threatening to the environment and human health, due to their bioaccumulative potential. Drugs, such as hydroxychloroquine, are part of this group [1].

Removing this type of contaminant from watercourses is extremely important for maintaining the health of aquatic life. Heterogeneous photocatalysis is an advanced oxidative process, which can contribute to the removal of this type of contaminant through the production of hydroxyl radicals (•OH) [2].

In photocatalysis, semiconductors are used to favor the production of these •OH, such as manganese ferrite ($MnFe_2O_4$), which has properties that favor its application under visible irradiation [3]. Reduced graphene oxide (G), in turn, ca be associated with this semiconductor to optimize its photocatalytic capacity, considering that it is a material with excellent properties [4].

Furthermore, these materials can also be associated with a support, aiming to improve the stability of the photocatalyst, as well as facilitating its recovery after the photocatalysis process. Bone char (CP) is an industrial waste that has the capacity to contribute to the efficiency of the photocatalytic system [5].

Therefore, the objective of this research was to evaluate the degradation efficiency of the heterostructured photocatalyst of $MnFe_2O_4$+G (GM) supported on CP, called CP-GM with different proportions of G (5%, 10% and 20%), in order to investigate the benefit of using carbonaceous material in the heterostructured photocatalyst, and its contribution to the efficiency of the photocatalytic process.

Material and Methods

The synthesis of the CP-GM heterostructured photocatalyst, and also the methodological procedure to evaluate its efficiency, was based on the methodologies described by Ferreira [6] e Bernardino [5].

For the photocatalytic test, a solution of hydroxochloroquine at 10 ppm was used, and the influence of the amount of G present in the photocatalyst on the drug removal efficiency was evaluated. For this, three materials were synthesized: CP-GM5 (with 5% G); CP-GM10 (with 10% G); CP-GM20 (with 20% G), which were applied at a concentration of 0.25 g/L during 120 min reaction. The three materials were tested under the same operating conditions.

The concentrations of the hydroxychloroquine solution were measured with the aid of an Agilent Car 60 UV-Vis spectrophotometer, adjusted to a wavelength of 343 nm and based on its calibration curve previously obtained at different concentrations, and the removal efficiency (%) was calculated according to Equation 1 [7].

$$\text{Removal efficiency } (\%) = \left(\frac{C_0 - C_f}{C_0}\right).100 \qquad (1)$$

Where C_0 is the initial concentration of hydroxychloroquine and C_f is the concentration at time t.

Results and Discussion

The results demonstrated in Figure 1 indicate that the material CP-GM20, with a higher concentration of G, reached a maximum efficiency of 46%, a value higher than the 37% and 36% achieved by the photocatalysts CP-GM10 and CP-GM5, respectively. It is possible to understand this result by analyzing the properties of $MnFe_2O_4$ and G, and their effects when they are combined.

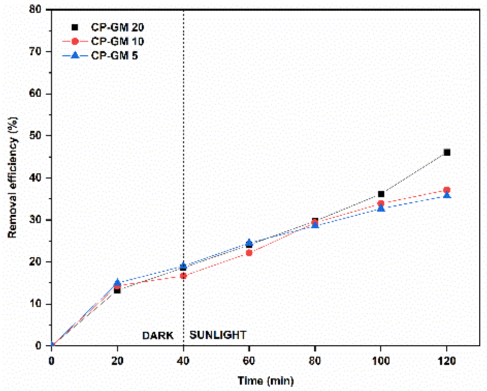

Figure 1. Removal efficiency of hidroxiclorochyne by CP-GM5, CP-GM10 e CP-GM20.

The $MnFe_2O_4$, is an excellent photocatalyst for visible irradiation sources, and one of its favorable properties for the process with sunlight is its narrow bad band gap (1.4–2.5 eV), and its excellent ability to transfer electrons (e^-) [3, 8]. However, this semiconductor has a high rate of recombination of electron(e^-)/hole(h^+) pairs, which impairs the formation of reactive radicals during the photocatalytic process [9].

The G is a carbonaceous material with unique properties that can actively contribute to the systems efficiency. This material, when associated with $MnFe_2O_4$, has the ability to act as an e^- receptor, which tends to reduce the rate of recombination of e^-/h^+ pairs in the semiconductor [10].

Keeping the h^+ photogenerated in $MnFe_2O_4$ available for longer during the process is advantageous for its efficiency, considering that it has the ability to directly attack polluting molecules, due to its high oxidative potentia [3].

Furthermore, these electrons photogenerated from $MnFe_2O_4$ and received by G, have the ability to react with oxygen and form more reactive radicals, such as the superoxide radical, which is also a powerful oxidant and can actively contribute to the system's efficiency [6].

Therefore, it is understood that the greater amount of graphene present in the CP-GM20 heterostructured photocatalyst improves the efficiency of the system, as it contributes to a reduction in the e^-/h^+ pair recombination rate, favors the formation of reactive radicals, and also prevents excessive agglomeration of $MnFe_2O_4$ nanoparticles, maintaining the abundance of active site.

Conclusions

From the obtained results, it is concluded that the heterostructured photocatalyst that presented the best results for removing the drug hydroxychloroquine was CP-GM20, with a greater amount of reduced graphene oxide (G). The result demonstrates that G contributes to the photocatalytic activity of the $MnFe_2O_4$ semiconductor, due to its properties, as ability to act as an e^- receptor, large surface area and and capacity that favors the formation of reactive radicals.

Acknowledgments

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