Photodegradation of hydroxychloroquine using manganese ferrite and reduced graphene oxide supported on bone char

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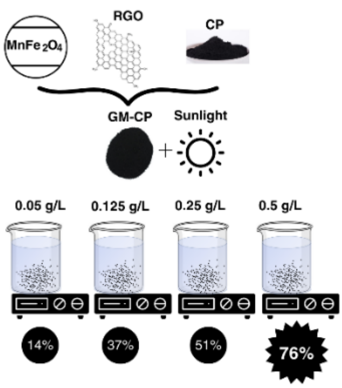

Research aimed at applying efficient technologies to remove persistent contaminants emerging from the aquatic environment, such as hydroxychloroquine, has been emerging recently. Heterogeneous photocatalysis is an advanced oxidative process that has the potential to contribute in this regard. Therefore, this research aimed to evaluate the efficiency of a reduced graphene oxide and manganese ferrite photocatalyst supported on bovine bone char, called GM-CP, with sunlight as an irradiation source, for photodegradation of the drug hydroxychloroquine. The photocatalyst was applied at different concentrations (0.05, 0.125, 0.25 and 0.5 g/L), and after 120 minutes of reaction, the system with the highest amount of GM-CP showed the best hydroxychloroquine removal result (76%).

Introduction

Hydroxychloroquine is a drug considered persistent and bioaccumulative, which makes it capable of reaching different types of organisms. Furthermore, its extensive use also raises concerns about its improper disposal, which can generate contaminated effluents and facilitate the contamination of water courses [1].

Therefore, the development of methodologies capable of completely removing emerging contaminants is necessary. Heterogeneous photocatalysis is an advanced oxidative process (AOP), which, like the others, aims to generate in situ reactive oxygen species with high oxidation capacity, such as the hydroxyl radical (•OH). In this process, solid semiconductors are used to convert light energy into chemical energy, which consequently induces redox reactions to form reactive radicals capable of oxidizing target pollutant molecules [2].

Manganese ferrite ($MnFe_2O_4$) is a promising semiconductor in the area of photocatalysis, as it presents some advantageous properties for the system, such as biocompatibility, magnetic susceptibility, stability and also a narrow band gap, a factor that favors its application under visible irradiation, allowing the use of sunlight [3].

Graphene and its derivatives, such as reduced graphene oxide (RGO), are carbonaceous materials with the potential to assist in this limitation of $MnFe_2O_4$, considering that they have properties such as large surface area, good chemical and thermal stability, good conductivity, good adsorption capacity and also act as a good electron acceptor, which optimizes the photocatalytic process [4].

To contribute to the stability of this heterostructured photocatalyst, bone char is an industrial waste that can be applied as a support. This support favors the adsorption of pollutant molecules, facilitating the attack of reactive radicals and, in addition, its composition assists in the photocatalytic process through the production of extra •OH [5].

Therefore, the present research aims to evaluate the photodegradation of the drug hydroxychloroquine, using different concentrations of the heterostructured photocatalyst of $MnFe_2O_4$-RGO, supported on bone char, called GM-CP.

Material and Methods

The synthesis of the GM-CP heterostructured photocatalyst, as well as the methodological procedure to evaluate its efficiency, was based on the methodologies described by [6] e Bernardino [7].

The main objective was to evaluate the removal of hydroxychloroquine, through the heterogeneous photocatalysis process, using different concentrations of the dispersed photocatalyst. For this, a hydroxychloroquine solution was used at a concentration of 10 ppm, where the photocatalyst GM-CP was dispersed at concentrations of 0.05, 0.125, 0.25 and 0.5 g/L separately, under the same conditions of operation.

The concentrations of hydroxychloroquine solutions were found using the Beer–Lambert law, which relates absorbance to concentration. 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 known concentrations of contaminant, it was possible to measure the absorbance of the solutions and then calculate their remaining concentration. . The removal efficiency was calculated according to Equation 1 [8, 9].

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

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

Results and Discussion

The removal efficiency of hydroxychloroquine by GM-CP was tested at different concentrations of the photocatalyst: 0.05, 0.125, 0.25 and 0.5 g/L, as shown in Figure 1.

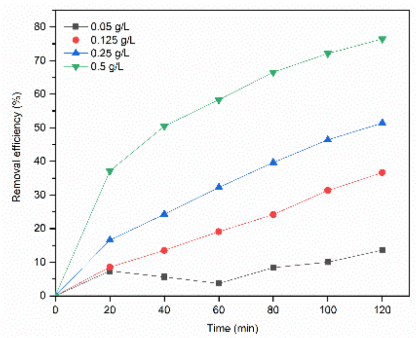

Figure 1. Removal efficiency of hidroxiclorochyne by GM-CP at different concentrations of dispersed photocatalyst

From the results obtained, it is possible to observe that the use of a higher concentration of photocatalyst favored the removal of hydroxychloroquine. When using 0.5 g/L, the removal efficiency after 120 min of reaction reached a value of 76%, an efficiency higher than the maximum removal of 51% when using a concentration of 0.25 g/L. This result is as expected, considering that with the use of a greater amount of photocatalyst, there is also an abundance of active sites available for the production of reactive radicals, as well as for the initial adsorption of hydroxychloroquine molecules. [7, 10].

Furthermore, another factor that probably favors the removal of hydroxochloriquine is the composition of the synthesized photocatalyst (GM-CP). The synthesized material contains iron oxide in its composition, a compound that during the photocatalytic process tends to transition between Fe^{2+} e Fe^{3+}, as demonstrated by equations 1 and 2, which favors the formation of reactive radicals, and consequently the degradation of organic compounds. [1, 3].

$$Fe^{3+} + H_2O + h\upsilon \rightarrow Fe^{2+} + \bullet OH + H^+ \quad (2)$$
$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + \bullet O^{2-} \quad (3)$$

Furthermore, bone char is rich in hydroxyapatite, which is an inorganic material with excellent adsorption capacity and the ability to carry out ion exchange of various compounds present in water, in addition to favoring the formation of reactive radicals [7]. Therefore, the higher concentration of photocatalyst improves the GM-CP photocatalytic performance, due to the favorable properties of the three materials that integrate the photocatalyst.

Conclusions

From the obtained results, it is concluded that the heterostructured photocatalyst GM-CP presented significant photocatalytic potential for removing the drug hydroxychloroquine. GM-CP performed better when used in greater quantities, as its abundance favors the formation of reactive radicals and consequently the removal of the contaminant. However, it is recommended that the material be tested at higher concentrations, seeking to know the saturation limit of the photocatalyst.

Acknowledgments

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