Photocatalysis of clonazepam from Fe_3O_4@GO under UV-C radiation

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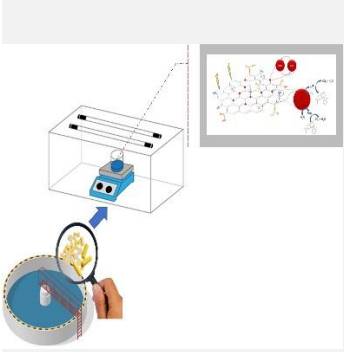

The presence of pharmaceutical components in surface waters has become a concern, hence there is no effective treatment for its degradation. In this study, heterogenous photo-Fenton process was employed for the treatment of clonazepam, with a magnetic photocatalyst. For this, graphene oxide was synthesized and functionalyzed with Fe_3O_4. Scanning electron microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) were performed to evaluate the surface and composition of the material. Kynetics of the photocatalytic process was carried out under UV-C radiation. Other radiation sources were tested. EDS analysis showed high material purity, SEM analysis indicated the success of the synthesis and functionalization process. Kinetics results showed the complete degradation of a 100 mL solution of 5 $mg.L^{-1}$ within 5 minutes. Compared to other processes, the system studied in this work presented the best degradation efficiency.

Introduction

One of the pharmaceutical sector's main concerns is the impact of its industrial activities on the environment and human health, since drugs can also produce the same biological response whether it gets to the target organism or not. [1]

Advanced oxidative processes (AOP) have been pointed as alternative effluent treatment techniques. One of the most used AOPs is the Fenton processes. These processes are characterized by the generation of •OH from the exposure of H_2O_2 to iron salts. Fenton's homogeneous process has disadvantages, such as continuous loss of iron ions. In heterogeneous Fenton processes, iron ions are supported in matrices, e. g., graphene oxide. These processes have the same principle as homogeneous processes, however, the production of •OH is catalyzed on the surface of the material [1;2;3].

The functionalization of GO with magnetite has been shown to be effective for degradation of several classes of contaminants, however, works with clonazepam are still rare in literature [4;5]

The present work aims to treat clonazepam via heterogeneous photo-Fenton process using an easy-to-recover magnetic photocatalyst.

Material and Methods

Graphene oxide was synthesized via modified Hummers method to obtain graphite oxide, followed by mechanical exfoliation to obtain GO [6;7]. The functionalization of graphene oxide with magnetite nanoparticles was carried according to a method proposed by da Silva et al. [5].

Scanning electron microscopy (SEM) was performed to evaluate the surface of Fe_3O_4, GO and Fe_3O_4@GO nanomaterials. The analysis was carried out on a microscope, integrated with the Energy Dispersive X-ray Spectroscopy (EDS) technique on a spectrometer for the analysis of elemental composition.

To test the photocatalytic capacity of the material, kinetics of the photocatalysis process was carried out under UV-C radiation. For this, 100 mL of a clonazepam solution at 5 $mg.L^{-1}$ and at a pH equal to 3 was placed in contact with 1.0 mg of Fe_3O_4@GO together with H_2O_2 at 15.0 $mg.L^{-1}$ for 15 minutes. The data were fitted to pseudo-first order (PFO) models, pseudo-second order (PSO).

CLZ concentration was determined using high performance liquid chromatography (HPLC) equipped with a UV-Visible detector. Separation was carried out on a C18 column using methanol and distilled water (v/v = 70/30) as mobile phase. The HPLC was operated at a flow rate of 1$mL.min^{-1}$ and the wavelength used was 254 nm.

The efficiency of the photo-Fenton reaction with Fe_3O_4@GO under UV-C radiation was compared with other processes. Other radiation sources were tested. The tests were carried under experimental conditions identical to the previous tests.

Results and Discussion

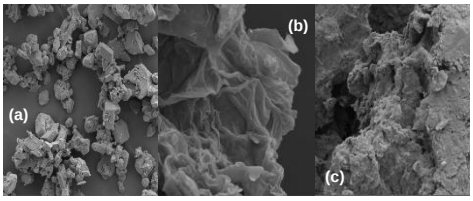

Figure 1. SEM images for Fe_3O_4 (a), GO (b) and Fe_3O_4@GO (c)

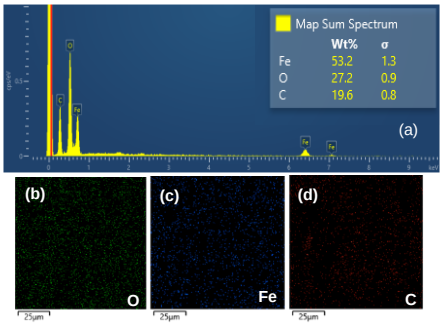

Figure 2. Energy dispersive x-ray pattern of Fe_3O_4@GO (a), (b-d) elemental mapping of elements O, Fe and C, respectively.

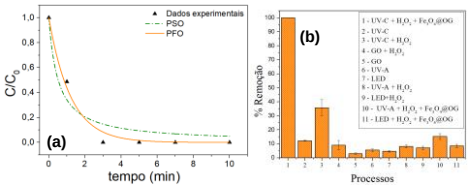

Figure 3. Kinetics of clonazepam photodegradation by Fe_3O_4/OG (a) and comparative study of processes (b)

The results in Figure 2 showed that Fe_3O_4@GO is composed of Fe (53 wt%), O (27 wt%) and C (20 wt%). This result highlights the purity of the material produced.

Figure 1.a shows the agglomeration of these nanomaterials, caused due to their magnetic nature. Studies have shown that the heterogeneous octahedral shape of Fe_3O_4 nanoparticles is related to the use of amine sources in their synthesis. In this study, NH_4OH was used during the synthesis of Fe_3O_4/GO, which would justify the morphology found in the SEM analyzes [8;9]. Figure 1.b shows the OG sheets with a smooth surface, different from Figure 1.c, where it can be seen that the Fe_3O_4/GO has a rough surface due to the deposition of Fe oxide nanoparticles on the OG surface.

Figure 3.a presents the results of the photodegradation kinetics of clonazepam under UV-C radiation catalyzed by Fe_3O_4/GO, where it can be seen the complete degradation of the pollutant after 5 minutes. The model that best fit the experimental data was the PFO model with a reaction rate constant of 0.83min^{-1} (R^2 = 0,99 e χ^2 0.002).

Figure 3.b presents the results of a comparative study of the degradation efficiency of clonazepam by different processes. In this graph it is possible to note that the system studied in this work presented the best drug degradation efficiency. Photo-peroxidation presented the second best result with 35.73% removal. The variation in results can be explained by the photocatalyst's role in facilitating additional reactions. Other radiation sources were not efficient in degrading the contaminant. For homogeneous processes, this can be justified by the fact that the generation of •OH from the photolysis of H_2O_2 is more efficient when irradiated at 254 nm. For processes with catalyst (10 and 11), the results are explained by the material's better affinity to UV-C radiation, also proven by UV-Visible reflectance spectroscopy [10].

Conclusions

Efforts to find alternative treatments for pharmaceutical contaminant degradation are essential, given the presence of these pollutants in various water matrices. In this work it was seen that Fe_3O_4/GO was able to degrade a 100 mL solution of 5 $mg.L^{-1}$ after 5 minutes. The efficiency of the proposed process was compared with other processes, in which the system studied in this work presented the best drug degradation efficiency. The functionalization of GO with magnetite made it easier to recover the nanomaterial at the end of the process.

Acknowledgments

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References

[1] T. Rasheed, M. Bial, F. Nabeel, M. Adeel, H. Iqbal, *Environment International*, 122 (2019) 52.
[2] D. Ma, H. Yi, C. Lai, X. Liu, X. Huo, Z. An, L. Li, Y. Fu, B. Li, M. Zhang, L. Qin, S. Liu, L. Yang, *Chemosphere,* 275 (2021)
[3] J. Ribeiro, M. Nunes, *Environmental Research*, 197 (2021)
[4] A. Baptisttella, C. Araujo, M. Silva, G. Nascimento, G. Costa, B. Nascimento, M. Ghislandi, M. da Motta Sobrinho, *Separation Science and Technology*, 56 (2021) 425
[5] M. Silva, Z. Souza, J. Cavalcanti, T. Fraga, M. da Motta Sobrinho, M. Ghislandi, *Environmental Science and Pollution Research,* 28 (2020) 23684.
[6] W. Hummers, R. Offeman, *Journal of the American Chemical Society,* 80 (1958) 6.
[7] T. Fraga, M. Silva, E. Freire, L. Almeida, M. da Motta Sobrinho, M. Ghislandi, M. Carvalho, *Chemical Engineering Research and Design,* 180 (2022) 109.
[8] G. Perez, M. Romero, E. Saitovitch, F. Litterst, J. Araujo, D. Bell, G. Solorzano, *Solid State Sciences,* 106 (2020)
[9] L. Norfolk, K. Kapusta, D. Cooke, S. Staniland, *Green Chemistry,* 23 (2021) 5724.
[10] H. Zhao, J. Wang, D. Zhang, Q. Dai, Q. Han, P. Du, C. Liu, Y. Xie, Y. Zhang, H. Cao, Z. Fan, *Scientific Reports,* 7 (2017).