

Adsorption of diclofenac by magnetic graphene oxide

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Abstract

The increasing detection of active pharmaceutical compounds in water bodies demonstrates the inefficiency of conventional processes in removing this class of contaminants and highlights the need for alternative treatment methods. Here, an adsorbent material based on graphene oxide functionalized with magnetite was synthesized, aiming to facilitate the recovery of the material at the end of the process. The Fe₃O₄/GO presented a pHPZC of 7.5 and a saturation magnetization of 0.22 emu.g⁻¹. Despite the low value, the material can be attracted when subjected to an external magnetic field. The magnetite precursor showed a saturation magnetization of 21 emu.g⁻¹. This difference was justified by the presence of GO in the adsorbent. The adsorption properties of Fe₃O₄/GO were tested with diclofenac. It was observed that the model that best fit the experimental data was the pseudo-second-order model, with an adsorption coefficient of 27.69 mg.g⁻¹ and a kinetic constant of 0.02 g.mg⁻¹.min⁻¹. These results were justified through an analysis of the medium's pH, the drug's dissociation constant, and the material's point of zero charge.

Keywords: Adsorption; diclofenac; emerging contaminants; magnetic graphene oxide.

1. Introduction

Pharmaceutical active compounds (PhaCs) are continuously released into the ecosystem due to their widespread use in daily life and the inefficiency of current wastewater treatment methods. Their presence in water bodies can cause numerous health and environmental issues due to their toxicity, bioaccumulation, and persistence, making them an increasing global concern [1, 2].

Conventional treatment methods are insufficient for removing these compounds from wastewater due to their properties, including lipophilicity, volatility, polarity, and persistence. Several alternative methods are available for removing pharmaceutical waste from water, such as adsorption techniques [3, 4].

In this context, a wide variety of materials have been used as adsorbents: many classified by authors as low-cost; others classified as high-capacity and selective materials [5].

Graphene oxide has been studied as an adsorbent for various types of contaminants. GO has a 2D structure similar to monolayer graphene; however,

the carbon atoms present in the basal plane of GO are covalently bonded to oxygen-containing groups such as hydroxyl, epoxy, and carbonyl, which provide GO with high colloidal stability in water [6, 7, 8]. The functionalization of GO allows for the tuning of properties and, consequently, an improvement in adsorption performance. Its combination with iron oxides, for example, enables better recovery of the material when exposed to an external magnetic field, allowing for its reuse [9, 10].

2. Methodology

2.1 Graphene oxide synthesis

Graphene oxide was synthesized by Hummers and Offeman method and modified according Fraga et al. (2018) [11].

2.2 Graphene oxide functionalization

Reduced titanium oxide was synthesized using the chemical reduction method similar to that proposed by Xing et al. (2013) and modified according da Silva et al. (2024) [12, 13].

2.3 Characterization

The determination of the point of zero charge pH (pH_{PZC}) was carried out using the salt addition method. For this, 0.1 g of Fe_3O_4/GO was mixed with 40.0 mL of NaCl for 24 hours. The pH of the salt solution was previously adjusted to specific values ranging from 2 to 12, using hydrochloric acid (HCl, 37% P.A., DINÂMICA) and sodium hydroxide (NaOH, Química Moderna) 1.0 mol.L⁻¹ and a pH meter model Q400as [14].

The magnetic properties of GO and Fe_3O_4/GO were investigated through hysteresis curves. For this, a vibrating sample magnetometer (VSM), model Av 7 (Microsense), was used.

2.4 Adsorption test

The adsorption capacity of Fe_3O_4/GO was investigated for the removal of diclofenac. For this, 200 mL of a diclofenac solution at 10 mg.L⁻¹ and at pH 6 was brought into contact with 10 mg of the material, remaining under agitation at 100 rpm for 60 minutes. During this period, aliquots were taken from the system, and the percentage of adsorption and the adsorption capacity were calculated. The experimental data were analyzed according to the pseudo-first-order and pseudo-second-order models.

3. Results

Fig 1 shows the point of zero charge pH (pH_{PZC}) of Fe_3O_4/GO , where it can be observed that the material has a pH_{PZC} of 7.5. This means that when the pH of the medium is lower than the pH_{PZC} , the surface of the nanomaterial is positively charged; on the other hand, when the pH of the medium is higher than the pH_{PZC} , the surface of Fe_3O_4/GO is negatively charged [9, 14]. This test is important to enable a complete understanding of the adsorption processes influenced by the charges of the material and the chemical state of the pollutant.

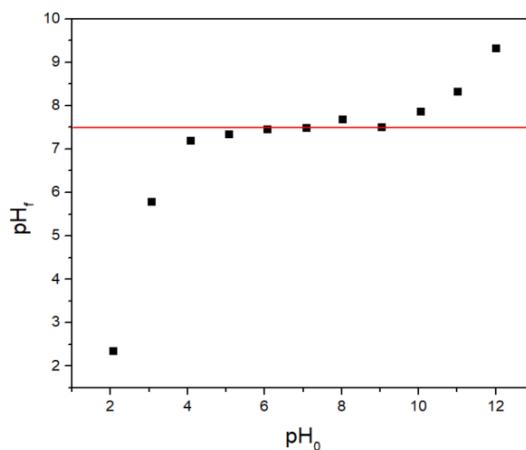


Fig. 1. Point of zero charge pH of Fe_3O_4/GO

In Fig. 2., it can be observed that the synthesized nanomaterial exhibits superparamagnetic properties. This is concluded from the absence of hysteresis in the curves. Additionally, it is evident that the saturation magnetization for Fe_3O_4 and Fe_3O_4/GO are 21 emu.g⁻¹ and 0.22 emu.g⁻¹, respectively. The difference between these results is attributed to the presence of GO, a non-magnetic material.

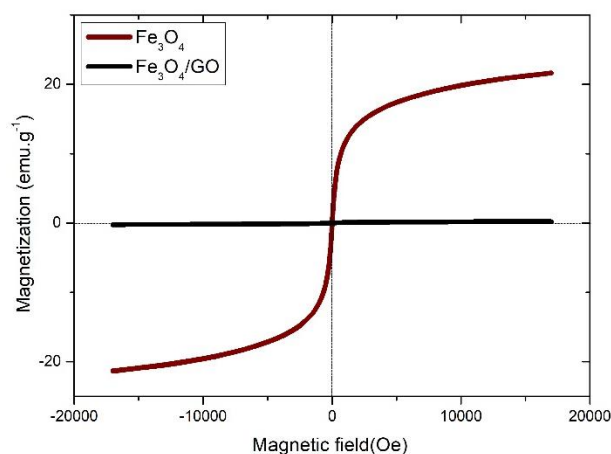


Fig. 2. Hysteresis curves of Fe_3O_4 and Fe_3O_4/GO

Despite the low saturation magnetization value, Fig 2 shows that Fe_3O_4/GO responds when exposed to an external magnetic field, allowing for the recovery of the nanomaterial.

A kinetic study was conducted to determine whether the synthesized material could adsorb diclofenac. Analyzing the results in Fig. 3 and Table 1, it can be observed that the model that best fit the

experimental data was the pseudo-second-order model.

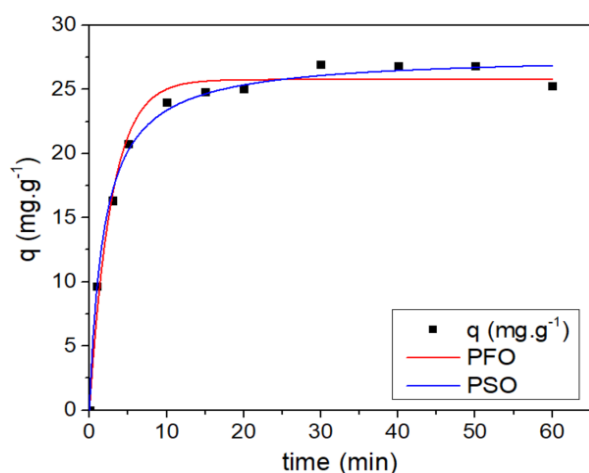


Fig. 3. Adsorption kinetics of diclofenac by $\text{Fe}_3\text{O}_4/\text{GO}$

Table 1. Kinetic parameters for the adsorption of diclofenac by $\text{Fe}_3\text{O}_4/\text{GO}$

Model	Parameter		Statistical Parameter	
PFO	q_{eq} (mg g^{-1})	k_1 (min^{-1})	R^2	χ^2
	25,77	0,35	0,98	1,18
PSO	q_{eq} (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2	χ^2
	27,69	0,02	0,99	0,55

Diclofenac has a pKa of 4.2; since the pH of the medium is higher than the drug's pKa, it is negatively charged, while the surface of the adsorbent is positively charged. Despite the experimental conditions favoring electrostatic attraction between the material and the contaminant, the maximum percentage of adsorbed diclofenac was approximately 15%.

4. Conclusion

The academic community's search for more efficient methods to treat emerging contaminants is of utmost importance given the polluting potential of this class of substances. In this work, the proposed method for synthesizing a graphene oxide-based adsorbent functionalized with magnetite proved effective in obtaining a

superparamagnetic material that responds quickly when placed under the influence of an external magnetic field. This property, attributed to the presence of iron oxide, allows for the rapid and easy recovery of the nanomaterial at the end of the process, enabling the material to be reused or properly disposed of when reuse is no longer possible.

The adsorption kinetics showed that, under the proposed conditions, 10 mg of $\text{Fe}_3\text{O}_4/\text{GO}$ adsorbed only 15% of diclofenac present in 200 mL of a solution at 10 mg.L^{-1} . It was observed that, due to the medium conditions, the material's pH_{PZC} , and the contaminant's pKa, electrostatic attraction was favored; however, the low removal percentage can be explained by the proximity of these three values. To promote electrostatic attraction between $\text{Fe}_3\text{O}_4/\text{GO}$ and diclofenac, the pH of the medium would need to be lower than the pH_{PZC} , where the material is positively charged, and higher than the pKa of diclofenac for the molecule to be negatively charged. Since the pKa of diclofenac is 4.2 and the pH_{PZC} is 7.5, the pH of the medium could only assume a very narrow range of values. Additionally, the kinetic model that best fit the experimental data was the PSO model, with a rate constant of $0.02 \text{ g.mg}^{-1} \text{ min}^{-1}$.

Despite this, the adsorption capacity of the nanomaterial under study could be optimized through a more in-depth investigation of the medium's conditions and other variables that influence the adsorption process.

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