Removal of caffeine from aqueous solutions with graphene oxide and metal nanoparticles adsorbents

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Abstract

Graphene is a two-dimensional material composed of carbon atoms with diverse applications, including as an adsorbent. However, its small particle size limits its effectiveness in removing water contaminants. To address this issue, a composite adsorbent combining graphene oxide, metal nanoparticles, and activated carbon can be developed for water treatment applications, particularly for removing micropollutants like caffeine, an emerging anthropogenic contaminant. This study aimed to evaluate an adsorbent made from activated carbon, graphene oxide, and copper and silver nanoparticles for its capacity to remove caffeine from water. After synthesizing graphene oxide, it was mixed with activated carbon derived from vegetable sources and modified with copper and silver nanoparticles. The resulting adsorbent was tested for its adsorption kinetics in an aqueous caffeine solution. The results demonstrated that using 0.1 g of the adsorbent without adjusting the solution pH could remove approximately 67% of the caffeine within 8 hours, fitting well with the Elovich model. It was concluded that while extended adsorption time increases removal efficiency, the developed adsorbent exhibits a high capacity for removing pharmaceuticals from water.

Keywords: caffeine; graphene oxide; metallic nanoparticles; adsorption; water treatment.

1. Introduction

The issue of emerging pollutants is gaining attention due to the long-term harm they can cause, as demonstrated by various studies [1]. Micropollutants, or emerging pollutants, are substances introduced into water bodies primarily through human activities. These contaminants, which include pharmaceuticals like caffeine, are continuously released into aquatic environments and are not eliminated by conventional water treatment processes [2].

Caffeine is increasingly recognized as a micropollutant in water due to its widespread consumption and subsequent release into the environment. Found in beverages, pharmaceuticals, and personal care products, caffeine enters water systems primarily through human waste and wastewater discharge [3]. Traditional water treatment processes often fail to remove caffeine effectively, allowing it to persist in aquatic environments. As a result, caffeine can impact water quality and pose potential risks to aquatic life and ecosystems. The presence of caffeine as a micropollutant highlights the need for advanced water treatment methods to ensure the removal of such contaminants [4].

There are several technologies studied that can remove caffeine from water, including adsorption. Adsorption is an effective technique due to its operational simplicity and relatively low cost. Through the application of different adsorbent materials, it is possible to treat water more effectively, reducing the presence of pharmaceuticals and other micropollutants, and contributing to environmental preservation and public health [5]. Among the adsorbents used is activated carbon, widely used due to its high surface area and adsorption capacity. Metal oxide nanoparticles, such as copper oxide and silver oxide, have shown potential in drug removal due to

their chemical properties and high specific surface area. In addition to these, graphene-based materials, such as graphene oxide, have been investigated for their high adsorption capacity and potential for chemical modification, allowing efficient drug removal [6].

In this context, the use of adsorbents based on graphene oxide and copper and silver nanoparticles supported on charcoal was evaluated to remove caffeine from contaminated water.

2. Methodology

The synthesis of graphene oxide (GO) was carried out using the hummers method modified by [7]. After this step, graphene oxide was impregnated into activated carbon of vegetable origin obtained by the company Purific according to [8] and [9]. GO in activated carbon was reduced (GOR) through exfoliation with ethylene glycol. Once this was done, the metal compounds were impregnated with GOR according to [10]. The material obtained was slowly cooled to room temperature, and then washed and filtered with deionized water and dried at 80°C for 20h, finally obtaining the final adsorbent material.

Batch adsorption tests were carried out on a shaking table (Tecnal TE-4200) at 25°C and 150 rpm. The adsorbent mass was evaluated varying from 10 to 100mg and with the best mass the pH was varied (natural, 4, 7 and 10). Based on the best results, the kinetics were carried out from 1h to 8h. After the adsorptive process, the samples were filtered through a cellulose acetate filter (Millipore) with 0.45 µm porosity. Caffeine concentrations were analyzed using a DR5000 spectrophotometer using a standard curve. From the experimental data, adsorption percentages, %RD (%), as well as adsorption capacities, qe (mg.g^{-1}), were calculated according to equations 1 and 2.

$$\%RD = \frac{(C_I - C_E) \, x \, 100}{C_I} \quad (1)$$

$$qe = \frac{(C_I - C_E) \, x \, V}{m} \quad (2)$$

Where C_I being the initial concentration and C_E being the equilibrium concentration (mg.L^{-1}), V being the volume of the solution (L), m being the mass (g) of adsorbent used.

3. Results and discussion

The adsorption capacity (qe) is directly related to the mass of the adsorbent used. As shown in Figure 1, the percentage of removal across different adsorbent masses remains relatively consistent (ranging from 92% to 99%). However, qe decreases as the adsorbent mass increases. This is because a greater adsorbent mass means that the available contaminant is spread across more adsorption sites, leading to less adsorption per unit mass. Therefore, to achieve satisfactory removal efficiency while avoiding excessive material use and optimizing operational costs, the minimum effective amount of 10 mg was selected.
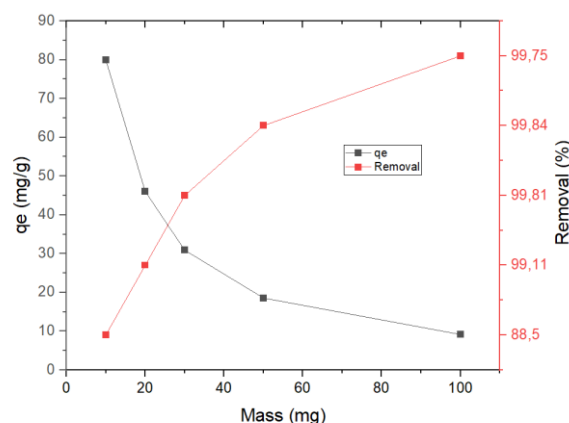

Fig. 1. Relationship between adsorbent mass and adsorption capacity and the influence of adsorbent mass on % removal.

Assessing pH is essential in adsorption studies because it significantly affects both the efficiency of the process and the interactions between the adsorbent and the adsorbate. As illustrated in Figure 2, the natural pH of the caffeine solution, around 5.7, resulted in a higher removal percentage (89%). Consequently, to optimize removal efficiency, solutions were used without altering the pH.
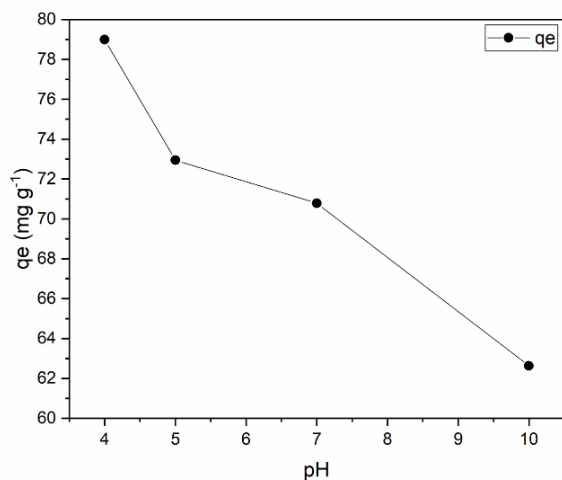
Fig. 2. Influence of solution pH on caffeine adsorption and removal.

Kinetics are used to determine the time required to reach adsorption equilibrium and to mathematically describe the behavior of the adsorption process over time. As shown in figure 3, equilibrium was reached in approximately 6.5 hours.

The Figure 3 demonstrated that the adsorption process was suitable for the different kinetic models evaluated. A good fit to the experimental data (Table 1) was observed for all models. The pseudo-firstorder and pseudo-second-order models, for example, showed good fit at the beginning and end points of the process, with a satisfactory correlation coefficient (R^2) of 0.95 and 0.97, respectively. However, the Elovich model was better suited to all points, including the intermediates, with a higher R^2 (0.98) and a lower χ^2 (8.66).
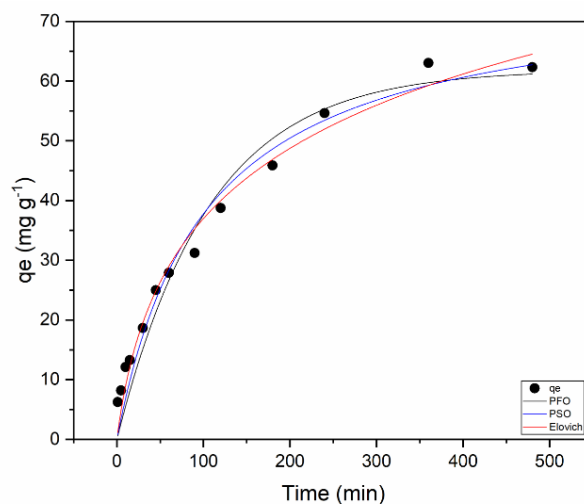

Fig. 3. Evaluation of experimental data for different kinetic models (pseudo-first order, pseudo-second order and Elovich).

Three mathematical models were used, pseudo-first order, pseudo-second order and Elovich, which were fitted to the experimental data. The kinetic parameters are shown in Table 1.

Table 1. Kinetic parameters of NR adsorption onto SB.

Model	Parameters	
Pseudo-first-order $q_t = q_e[1 - e^{-k_1 t}]$	qt (mg g-1)	61.87 ± 3.40
	K1 (h-1)	0.009 ± 0.001
	R²	0.95
	χ^2	19.73
Pseudo-second-order $q_t = \dfrac{k_2 q_e^2 t}{1 + k_2 q_e t}$	qt (mg g-1)	75.95 ± 4.74
	K_2 (h^{-1})	$1.30^{-4} \pm 2.94^{-5}$
	R²	0.97
	χ^2	13.25
Elovich	a (mg g^{-1} min)	1.14 ± 0.17

$q_t = \dfrac{1}{b}\ln a\,b + \dfrac{1}{b}\ln t$	b (mg g^{-1})	0.05 ± 0.005
	R^2	0.98
	χ^2	8.66

4. Conclusion

Concluded that the adsorption kinetics should be extended until equilibrium is reached to fully understand the caffeine removal process, whether it involves external diffusion, intraparticle diffusion, or chemical reactions. However, identifying the minimum adsorbent mass and the optimal pH for the solution can help optimize the adsorption process. Ultimately, the developed adsorbent demonstrated a high potential for caffeine removal in water treatment applications.

Acknowledgements

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