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Use of Natural Zeolite as a Low-Cost Adsorbent for the Adsorption of Fluoxetine in Aqueous Media

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Abstract

Zeolite, in particular, has been widely used in various sectors, especially in environmental control. The primary objective of this study is to investigate the use of natural zeolite as an adsorbent for the adsorption of the pharmaceutical compound fluoxetine in aqueous media. Adsorption studies were conducted, focusing on kinetics and isotherms. In the kinetic study, data were fitted to kinetic parameters, with the Elovich model providing the best fit, as indicated by the R^2 value. This suggests that chemisorption is the main factor in the adsorption of fluoxetine, with a maximum adsorption capacity of approximately 15 mg g^{-1}. For the adsorption isotherm, the data were well represented by the Langmuir, Freundlich, and Sips models, indicating that the adsorption process involves both chemisorption and physisorption. Based on these results, zeolite shows promise as an adsorbent for a wide range of contaminants, particularly due to its availability, efficiency, and low cost.

Keywords: Zeolite; Adsorption; Fluoxetine.

1. Introduction

Pollution by emerging contaminants (ECs), such as pharmaceuticals, has become a significant environmental threat, as these contaminants can reach the top of the food chain, posing a risk to human health. In light of this scenario, the issue of emerging contaminants has gained prominence, driving the development of new treatment technologies aimed at reducing the concentration and/or removal of these contaminants to acceptable levels, thereby minimizing their impact on both the environment and human health. These contaminants are widespread in the environment and have been detected in water supply sources, groundwater, and even in drinking water [1]. Research focused on the removal of emerging contaminants is gaining attention due to the non-biodegradable, persistent, and toxic nature of these substances, which tend to bioaccumulate in living organisms, causing various diseases and disorders [2].

In the field of antidepressant drugs, one of the most well-known is fluoxetine, which has been proven highly effective in treating depressive disorders. The major environmental concern is that fluoxetine, present in aqueous media, is hydrophilic and soluble. Studies indicate that it is the most frequently detected pharmaceutical in water bodies through the effluent from wastewater treatment plants (WWTPs), where conventional physical and biological treatment processes are inadequate for its removal [3,4]. Various techniques can be employed to reduce and/or remove ECs present in aqueous media, including adsorption, coagulation, filtration, and photochemical methods, among others. However, adsorption stands out in studies due to its low energy cost, efficiency, and the controllable parameters it offers [5,6].

Thus, the use of zeolites can be economically viable since they are abundant minerals with relatively low cost. In particular, the use of natural zeolite has been confirmed as an important practice in the environmental management of industrial waste. Results from industrial applications [7,8] confirm the potential of zeolitic material samples, especially considering their low-cost usage compared to other traditional processes.

The main objective of this study is to remove the pharmaceutical fluoxetine from aqueous media using natural zeolites.

2. Materials and Methods

2.1 Materials

The natural zeolites used in this study were commercially supplied by Celta Brasil®. The fluoxetine pharmaceutical was obtained from a compounding pharmacy with a high purity of >99%.

2.2 Characterization

The point of zero charge was determined using the '11-point' method (pH_{pzc}) [9].

2.3 Adsorption Kinetics

For the kinetic studies, a constant mass of 20 mg of zeolite was used as the adsorbent, with 30 mL of fluoxetine solution at a concentration of 60 mg L^{-1} as the adsorbate. Constant stirring at 150 rpm and an ambient temperature of 25°C (± 2°C) were maintained. Samples were collected at different time intervals for analysis.

The concentrations of Fluoxetine were measured using a UV-VIS DR500 spectrophotometer from HACH (London, UK) at a wavelength of 226 nm. A calibration curve was constructed for the measurements.

The models were fitted to the pseudo-first-order model (eq. 1), pseudo-second-order model (eq. 2) and Elovich model (eq. 3) using OriginPro 2019b software for obtaining graphs and statistical analysis.

$$qt = qe(1-e^{(-k_1 t)}) \qquad \text{(Equation 1)}$$

$$qt = \frac{k_2 qe^2 t}{1+k_2 qe t} \qquad \text{(Equation 2)}$$

$$qt = \frac{1}{\beta}\ln(1 + \alpha\beta t) \qquad \text{(Equation 3)}$$

Where:

qt = amount of adsorbed adsorbate (mg g^{-1}) at time t (min).
qe = equilibrium and the maximum adsorption capacities (mg g^{-1}).
k_1 = adsorption rate constant (min^{-1}).
k_2 = adsorption rate constant (g mg^{-1} min^{-1}).
A = initial adsorption rate (mg g^{-1} min^{-1}).
B = adsorption constant (mg g^{-1}).

2.4 Adsorption Isotherms

For the isotherm studies, the conditions were nearly identical to those used in the kinetic experiments. However, the concentration of fluoxetine was varied, and the agitation time was fixed at 240 minutes. For this study, Langmuir (eq. 4), Freundlich (eq. 5), and Sips (eq. 6) models were evaluated.

$$qe=\frac{Qmax\ K1Ce}{1+KlCe} \qquad \text{(Equation 4)}$$

$$qe=Kf\ Ce^{1/n} \qquad \text{(Equation 5)}$$

$$qe=\frac{Q_{max}(Ks\ Ce)^n}{1+(Ks\ Ce)^n} \qquad \text{(Equation 6)}$$

Where:
Q_{max} = maximum adsorption capacity, mg g^{-1}.
qe = amount of adsorbate concentration in the solid phase in equilibrium, mg g^{-1}.
Ce = amount of adsorbate concentration in the liquid phase, mg L^{-1}.
Kl = equilibrium constant, affinity between adsorbate and adsorbent, L mg^{-1}.
Kf = Freundlich constant relates the adsorption capacity and number of adsorption sites, L mg^{-1}.
N = that relates the intensity of the adsorption process (affinity between adsorbent and adsorbate).
Ks = sips constant, with the adsorption energy, L mg^{-1}.

3. Results and Discussion

3.1 Characterization

The point of zero charge (pH_{pzc}) for the zeolite was found to be 6.06. Previous studies using natural zeolite reported values close to this, around 6.2. Within the initial pH range of 5 to 9, the surface charge was zero, indicating that changes in pH did not interfere with the surface charge. Below pH 5, the adsorbent acquires a positive charge, while above pH 9, it acquires a negative charge [10].

3.2 Adsorption Kinetics

According to Figure 1, the highest fluoxetine adsorption capacity occurs within the first minutes due to electron exchange capacity and the formation of chemical bonds, reaching approximately 6 mg g^{-1} within the first hour. Subsequently, adsorption proceeds at a slower rate, entering the adsorption limiting phase until stabilization at 240 minutes, with a maximum capacity of 12 mg g^{-1}.

[11] Using zeolites as adsorbents for dye adsorption, kinetic studies showed a faster adsorption rate during the initial phase, followed by slower adsorption until stabilization, with maximum capacities ranging from 0.86 to 9.89 mg g^{-1}.

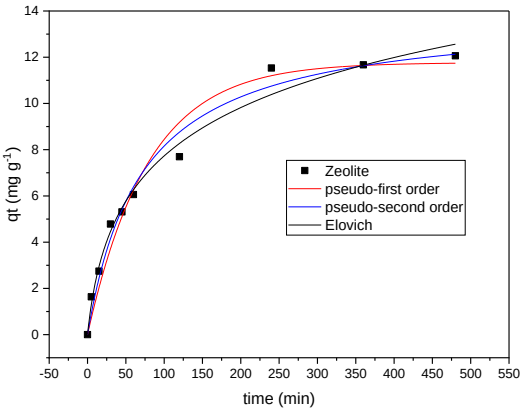

Fig. 1. Fluoxetine adsorption kinetic from Zeolite

The kinetic models were fitted to the data, and according to Table 1, the Elovich model provided the best fit compared to the others, with an R^2 value of 0.986. This indicates that chemisorption is the predominant factor in the interaction between the adsorbent and the adsorbate.

3.3 Adsorption Isotherms

To determine the maximum adsorption capacity, adsorption isotherms were conducted. Based on the obtained data, three mathematical models were selected: Langmuir, Freundlich, and Sips. The data are presented in Figure 2 and the statistical results in Table 2.

The adsorption capacity varies according to the initial concentration of fluoxetine in the sample, which is a determining factor. The three presented models fit the data well, indicating that adsorption occurs through both chemisorption and physisorption.

Table 1. Kinetic parameters of Fluoxetine adsorption.

Model		
Pseudo-first order	qt (mg g^{-1})	11.76
	k1 (min^{-1})	0.012
	R^2	0.97
	Adj. R^2	0.966
Pseudo-second order	qt (mg g^{-1})	13.91
	k2 (g mg^{-1} min^{-1})	0.001
	R^2	0.982
	Adj. R^2	0.98
Elovich	A (g mg^{-1} min^{-1})	0.32
	B (mg g^{-1})	0.308
	R^2	0.986
	Adj. R^2	0.985

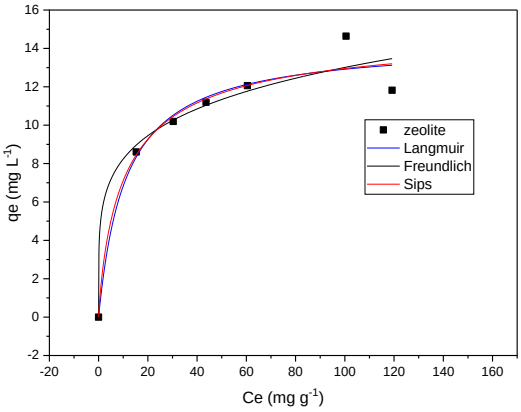

Fig. 2. Fluoxetine adsorption isotherm from Zeolite

Table 2. Isotherm model fitting parameters.

Model		
Langmuir	Kl (L mg^{-1})	0.091
	Qmax (mg g^{-1})	14.33
	R^2	0.962
Freundlich	Kf (L mg^{-1})	5.21
	n	5.04
	R^2	0.967
Sips	Ks (L mg^{-1})	0.088
	Qmax (mg g^{-1})	15.02
	n	0.84
	R^2	0.963

In this study, the maximum adsorption capacity (Qmax) was approximately 15 mg g^{-1}. Similar research using synthetic zeolites to adsorb fluoxetine from aqueous media reported results comparable to those of this study [12].

4. Conclusions

In this study, a natural adsorbent (zeolite) was used for the adsorption of the pharmaceutical fluoxetine in aqueous media. Based on the obtained analyses, the following conclusions were drawn:

- The point of zero charge (pHpzc) was close to neutrality, similar to other studies, which favors a broad range of contaminants that could be used as adsorbates.
- Kinetic data were fitted to mathematical models, with the Elovich model showing the best fit, indicating that chemisorption was the primary factor, although some physisorption also occurred.
- The adsorption isotherms showed that the models fitted to the obtained data had very close R^2 values, indicating that both chemisorption and physisorption processes were occurring, with Qmax reaching 15 mg g^{-1}.
- As a low-cost natural adsorbent, zeolite proves to be promising for future studies.

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