Evaluation of diazepam adsorption in aqueous media using low-cost and natural zeolite: equilibrium and kinetics

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Abstract

Diazepam has been detected in water sources around the world affecting the quality of drinking water. Even in small quantities, recent studies have proven the negative effects of the drug on human body. Since traditional water and sewage treatment do not remove this type of contaminant, it became interesting to evaluate forms to remove them from water sources. A cheap and eco-friendly alternative to remove this drug from the water is through adsorption using the natural clinoptilolite zeolite as an adsorbent. This work goal was to study the characterizations of clinoptilolite, such as scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffractometer (XRD), and Fourier transform infrared spectroscopy (FTIR) and analyze the potential of this material as an adsorbent. Kinetic studies and isotherm analysis were performed in batch. The results showed the potential of the natural zeolite to remove the pollutant in an aqueous medium reaching a maximum adsorption capacity of 8.25 mg g^{-1} . The adsorption process followed a pseudo-second-order kinetics indicating that the adsorption was based on a chemisorption process. The isotherms curves shown favorable adsorption and the Langmuir isotherm model fit the experimental data better.

Keywords Natural zeolite · Clinoptilolite · Characterization · Adsorption · PADs · Isotherm

Introduction

The contamination of water arrays by persistent and toxic compounds causes great concern in the scientific community since the risk that these substances represent to the environment. Among these contaminants, psychoactive drugs (PADs) are considered the most concentrated and frequently detected contaminants in various environmental matrices (Thiebault and Boussafir 2019).

One of the most applied PADs in medicine is the benzodiazepine diazepam (DZP), frequently used in the treatment of seizures, anxiety, muscle spasms, and insomnia, and it is one of the most dangerous compounds, due to its ability to bioaccumulate and generate toxic metabolites. Therefore,

chronic exposure to this drug has been studied in aquatic organisms and shows negative effects even at low concentrations (Laws et al. 2011; Luján-Facundo et al. 2019). In addition, the problem involving DZP can be aggravated by the growing consumption of anxiolytic drugs, especially during the COVID-19 pandemic, in which the effect of quarantine and social isolation caused an increase in cases of anxiety, insomnia, and depression in the population generally (Saidi et al. 2021; Wu et al. 2021).

It is also worth noting that the DZP is on the model list of essential drugs of the world health organization for pain and anxiety control (Pettus et al. 2020). In this sense, the increased consumption of DZP, associated with its incomplete removal in wastewater treatment plants (WWTPs) (Gao et al. 2012; Organización Mundial de la Salud (OMS) 2019) leads the study of efficient and economically viable solutions that can improve the treatment of wastewater treatment plants. Among the techniques already used, the adsorption process is notable because of its generally low cost, ease of operation, and high efficiency (Fakhri and Adami 2014; Sani et al. 2016, 2017; Saleh 2020, 2021). However, for its effectiveness and viability, it is necessary to choose a low-cost

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adsorbent, with high adsorption capacity and selectivity (Thiebault and Boussafir 2019).

In this context, the natural clinoptilolite zeolite becomes a potential adsorbent, as it is a hydrophilic material with a promising adsorption capacity along with high abundance and relatively low costs and has been the object of study for different organic molecules (Lam et al. 1998, 2001; Mohseni et al. 2016). Therefore, this natural material may be a suitable candidate for the adsorption of the drug DZP in its natural form.

The adsorption of the drug diazepam was investigated in adsorbents, such as clay minerals (Thiebault and Boussafir 2019; Thiebault et al. 2019), hydrogel (Mota and Fajardo 2021), and activated carbon (Sulaiman et al. 2016; Luján-Facundo et al. 2019). The use of zeolite CP in the removal of DZP has not yet been investigated. In addition to being natural, the use of CP as adsorbent does not require several changes in its structure. Therefore, the study of the efficiency of this material as an adsorbent in the removal of DZP from aqueous solutions under different conditions is of great importance, especially the study of the efficiency of this material as an adsorbent in the removal of DZP from aqueous solutions under different conditions.

From the above, the aim of this study is to investigate the use of the natural zeolite CP as an adsorbent for the removal of the benzodiazepine DZP in an aqueous system and to evaluate important process parameters, which are the adsorption equilibrium and the process kinetics and isotherms.

Materials and methods

The natural zeolite used as adsorbent was kindly provided by Celta Brasil, which is located on Vila Jovina-Cotia/SP, 06,705,150. It was a clinoptilolite type mainly composed of SiO₂ and Al₂O₃. Diazepam (99%) was obtained from Sigma-Aldrich. The adsorption tests were run with distilled water.

Preparation and characterization of the adsorbent

Before the experimental tests, the zeolite was washed with deionized water in an ultrasound bath to remove the impurities, and oven dried and sieved (0.4–1.0 mm). The CP zeolite was characterized from textural analysis through N₂ physisorption at 77 K, using Micromeritics (model: ASAP 2020), using approximately 0.1 g of degassed zeolite at 300 °C for a period of 12 h. The X-ray diffraction analysis was performed in a Bruker brand diffractometer, with an ion source copper scan speed of 2.0° 2 θ /min, from 5 to 65° 2 θ , with a step size of 0.01°, voltage of 40 kV, and 30-mA current. Infrared spectroscopy (FTIR) analysis was performed in a Bruker-Vertex 70 spectrophotometer in the range of 4000

to 400 cm⁻¹ with 100 scans and a resolution of 4 cm⁻¹. KBr was used as a reference, 100% transmittance, and for the analysis, 0.002 g of sample was weighed and mixed in 0.198 g of KBr. To visualize the morphology of the samples of adsorbents, a scanning electron microscope Shimadzu SS-550 Superscan SS-550 software was used. For a qualitative analysis of how the chemical elements are distributed on the surface of the material, the EDS technique coupled to a scanning electron microscope was used.

Adsorption experiments

The adsorption experiments were carried out in batch and performed in triplicate, which makes the results more reliable. A shaker table was used (Shaker Cientec CT/712R) with a stirring speed of 200 rpm, temperature of 28 °C, 50 mL of DZP solution as adsorbate, and 0.1 g of CP zeolite as an adsorbent. The aliquots of each experiment were filtered using a stainless-steel holder and 0.22- μ m membranes, supplied by Millipore. The spectrophotometric analyzes were performed in a Shimadzu UV–VIS spectrophotometer (model UV-1800), through the calibration curve obtained at different concentrations of DZP and read through the absorbance at the maximum wavelength of 230 nm and determined by its respective calibration curve. The adsorbed amount was determined by the difference between the final and initial concentration of DZP using Eq. 1.

$$q_t = \frac{(C_0 - C_e)V}{m_a} \quad (1)$$

where q_t is the amount adsorbed per gram of adsorbent at equilibrium (mg g⁻¹), C_0 is the initial concentration of adsorbate (mg L⁻¹), C_e is the concentration of adsorbate at equilibrium (mg L⁻¹), V is the volume of solution (L), and m_a is the mass of adsorbent (g).

To determine the adsorption kinetics of DZP in zeolite CP, a volume of 50 mL of solution with a concentration of 25 mg L⁻¹ of the contaminant and a mass of 0.1 g of zeolite, with removal of aliquots at time intervals, was used until the process reached equilibrium. The experimental data were applied to the non-linear kinetic adsorption models (Table S1) of pseudo-first-order (ESM Eq. 2), pseudo-second-order (ESM Eq. 3), Elovich (ESM Eq. 4), and the intraparticle diffusion model (ESM Eq. 5).

The adsorption isotherms were obtained by varying the contaminant concentration (1, 3, 5, 7, 10, 15, 20, and 25 mg L⁻¹) and applying 0.1 g of CP zeolite for each concentration. The results obtained were fitted to the non-linear isotherm models (Table S2) of Langmuir (ESM Eqs. 6 and 7), Freundlich (ESM Eq. 8), and Dubinin-Radushkevich (ESM Eqs. 9, 10, and 11).

Fig. 1 SEM images of the clinoptilolite sample: **a** 5000 $\times$, 500 μm ; and **b** 10,000 $\times$, 20 μm

Results and discussion

SEM

The morphological surface of the CP made by SEM analysis is represented in Fig. 1a. It can be observed that the material does not present any standard structural organization such as expected. It is also possible to observe that the material has small cavities, represented by bright spots in Fig. 1b (Saleh 2015; Kussainova et al. 2019; Güngör and Özen 2021). The EDS analysis provides the percentage of components found on the surface of the material (A. Saleh and K. Gupta 2012) and is depicted in Fig. 2. The presence of expressive peaks of Si, O, and Al was detected, which confirms the main compounds of zeolite, but once this material was found in nature the presence of other elements is also expected, such as Na (Tran et al. 2019).

XDR

The XRD pattern of the clinoptilolite sample is presented in Fig. 3. Through X'Pert Highscore Plus Software, it was possible to identify the crystal structure and quantify

the purity of the material. According to the Rietveld method, the characteristics peaks $2\theta = 9.8, 11.1, 22.3, 22.7, 26.0, 28.1, 30.0,$ and 32.0° of the sample diffractogram matched with Clinoptilolite (JCPDS sheet no. 00–025–1349), whose chemical formula is $(\text{Na}, \text{K}, \text{Ca})_6(\text{Si}, \text{Al})_{36}\text{O}_{72} \cdot 20\text{H}_2\text{O}$, and is in accordance with literature (Gottardi and Galli 1985; da Silva et al. 2021). Besides clinoptilolite, mordenite appeared as the second main phase, with 71.04% of clinoptilolite and 11.57% of mordenite. The material is monoclinic with the lattice unit cell parameters and has the following measurements: $a = 17.6 \pm 0.01 \text{ \AA}$, $b = 17.9 \pm 0.01 \text{ \AA}$, $c = 7.39 \pm 0.02 \text{ \AA}$, and $\beta = 116.0 \pm 0.008^\circ$. The analysis also confirms the material as a mineral and inorganic zeolite.

FTIR

The infrared spectrum was used to identify the functional groups present in the zeolite by their specific vibration. (Saleh 2011) Through Fig. 4, it is possible to notice a band in the range of $3640\text{--}3620 \text{ cm}^{-1}$ that can be associated with the vibration of free O–H groups represented by water (Kavak and Ülkü 2013). In the range of $1750\text{--}1600 \text{ cm}^{-1}$, it is noticed that the presence of vibration due to the presence

Fig. 2 EDS analysis of the natural zeolite CP

Fig. 3 XDR pattern of the zeolite clinoptilolite

of water adsorbed (Saleh 2018). The most intensive vibration frequency is between 1060 and 1040 cm^{-1} , which is a result of the structural units of the alumina-silicate lattice Si (Al)–O of the zeolite, which confirms the main composition of the material used in this study (Favvas et al. 2016). In the range of 470 – 460 cm^{-1} a characteristic vibration of bicyclo-vibration of O–Si–O or O–Al–O was observed (Demirbükür Kavak and Ülkü 2015).

Textural properties

The values obtained for the specific area, pore-volume, pore diameters, and zero-point charge are shown in Table 1. The value for the specific area of the material

Fig. 4 FTIR spectra of the zeolite CP sample

Table 1 Texture parameters of the clinoptilolite sample

Sample	S_{BET} (m^2/g)	V (cm^3/g)	d (nm)	pH_{ZCP}
Clinoptilolite	131.17	0.083	2.5	7.2

was $128.12\text{ m}^2/\text{g}$, a value higher than other studies that also used clinoptilolite zeolite (Akgül et al. 2006; Kennedy et al. 2019); this can be explained due to the variation of material characteristics accordingly with the region in which it is extracted. The pore diameter value indicates that it is a material with a predominantly mesoporous characteristic. However, according to the literature, clinoptilolite zeolite also presents characteristics of microporous adsorbents, in which there is a certain amount of impurities, especially clays, quartz, and amorphous vitreous material (Hernández et al. 2000). Regarding the pH_{ZCP} of the CP reaching a value of 7.2, it favors the adsorption of the DZP since the aqueous solution of DZP has a pH of 5.82 (da Silva et al. 2021).

Kinetics of adsorption

In Table 2 and Fig. 5a, the results of the adsorption kinetics of diazepam on CP natural zeolite are presented. The aim of the kinetic study is to determine the control mechanisms

Table 2 Parameters and determination coefficients of the non-linear kinetic models for diazepam adsorption

Model	Parameter	Temperature (K) 298
Pseudo-first order	k_1 (min^{-1})	0.013
	q_e (mg g^{-1})	8.862
	χ^2	0.124
	R^2	0.989
	R^2 adj	0.988
Pseudo-second order	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.001
	q_e (mg g^{-1})	10.63
	χ^2	0.047
	R^2	0.996
	R^2 adj	0.995
Elovich	α ($\text{mg g}^{-1} \text{min}^{-1}$)	0.277
	β (g mg^{-1})	0.404
	χ^2	0.186
	R^2	0.960
	R^2 adj	0.959
Intraparticle diffusion	K ($\text{mg g}^{-1} \text{min}^{-0.5}$)	1.957
	C (mg g^{-1})	0.989
	χ^2	0.007
	R^2	0.907
	R^2 adj	0.898

Fig. 5 Kinetic curve for adsorption of diazepam on CP zeolite at 298 K with fit to the **a** pseudo-first-order, pseudo-second-order, and Elovich models, and **b** fit to the intraparticle diffusion model

of adsorption processes (processes such as surface adsorption, chemical reaction) or diffusion mechanisms and also to determine the time needed to complete the adsorption process and its speed, which is useful for design models for the process. It is possible to observe that in the studied process, the adsorption occurred more intensely in the first 60 min, due to the greater availability of sites on the zeolite surface, and the equilibrium of the adsorption process is reached around 300 min. The shape of the kinetic shows the affinity between the adsorbent and the adsorbate.

According to the results of the kinetic studies, it can be verified that the adsorption kinetics of diazepam by zeolite CP can be better described by the pseudo-second-order kinetics model, according to the calculated statistical parameters, available in Table 2. This indicates that the adsorption process is based on a chemisorption process of diazepam present in the aqueous solution to the surface of the adsorbent, due to a physical–chemical interaction, since the hydrophilic characteristic of the zeolite favors this type of interaction (Gupta et al. 2018).

The intraparticle diffusion model is used to understand the mechanisms that may be involved in the adsorption process. Figure 5b shows the fit of the intraparticle diffusion model for adsorption of diazepam on zeolite CP, in which it is possible to visualize a multilinearity in the adsorption process, indicating that two or more steps can occur and that the intraparticle diffusion mechanism is not dominant. The first step between 0 and 10 min^{1/2} refers to the boundary layer effect, with external mass transfer, in which DZP is rapidly adsorbed by the CP zeolite. The second step concerns the diffusion of molecules to the adsorbent's innermost adsorption sites. Finally, in the last

step, there is an equilibrium where intraparticle diffusion decreases due to the low concentration of solute in the solution as well as lower availability of sites for adsorption (Calisto et al. 2019; Babas et al. 2021).

Adsorption isotherms

To investigate the phenomena that occurred at the surface of CP during the adsorption process, three models were applied: Langmuir, Freundlich, and Dubinin-Radushkevich. Figure 6 shows the equilibrium isotherms obtained

Fig. 6 Equilibrium isotherms for DZP adsorption at temperatures of 298, 303, and 308 K

for temperatures of 298, 303, and 308 K. It is possible to observe that due to a strong influence of temperature, showing that the adsorption of DZP consists of an endothermic process.

The fitting plots for each isotherm model are shown in Fig. 6 and it is possible to see an L1 type of isotherm according to (Giles et al. 1964) which configures that the ratio between the concentration of the compound in the solution and adsorbed on the solid decreases when the concentration of solute increases.

The calculated parameters summarized in Table 3 indicates that Freundlich and Dubinin-Radushkevich models did not fit as well as Langmuir, which reached a good correlation coefficient (R^2) and also presented a lower value of chi-square (χ^2) indicating that this model brings a better approximation between theoretical and experimental data. The better adjustment of the experimental data for the Langmuir isotherm model suggests that the adsorbent used exhibits finite numbers of identical active sites available for interaction with the adsorbate and there is no side interaction due to steric hindrance between the adsorbed molecules on the surface (Paudyal et al. 2020). It is also worth mentioning that the values referring to the k_L parameter increased with temperature, indicating that the temperature favored adsorption (Ghabbour and Davies 2011; Mohseni et al. 2016).

The parameter n of the Freundlich model at all 3 temperatures still indicates that the adsorption process was

strongly favorable under the investigated conditions, demonstrating the affinity between the adsorbent and adsorbate. Furthermore, the calculated values of $1/n > 1$ suggest that the adsorbent works well for solutions with a high concentration of the contaminant (Sarat Chandra et al. 2015).

Regarding the parameters calculated on D-R model, it can be noticed that the values obtained for E , for all temperatures tested, were below 8 kJ mol^{-1} indicating that the adsorption process of DZP on CP was of physical nature (Sari and Tuzen 2009).

Conclusion

The present study suggests that a natural clinoptilolite can be effectively used as an adsorbent for the removal of psychotropic drug diazepam from aqueous matrices. In this study, the importance of clinoptilolite morphology in the use of the adsorption process is clear and also confirmed through SEM, FTIR, and XDR analysis. According to the calculations, the adsorbed amount of the contaminant ranged from 8.05 to 8.25 mg g^{-1} . The kinetic model of pseudo-second-order fits better to the experimental data, indicating that it is a process with contribution of chemisorption. Langmuir was the isotherm model that best fit the experimental equilibrium data, whose parameters showed that it is strongly favorable adsorption.

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Data Availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

Table 3 Parameters and coefficients of the non-linear isotherms for DZP adsorption

Model	Parameters	Temperature (K)		
		298	303	308
Langmuir	$Q_{\max}$ (mg g^{-1})	8.051	8.348	8.259
	k_L (L mg^{-1})	0.344	0.684	1.823
	R_L	0.373	0.979	0.847
	R^2	0.990	0.980	0.972
	R^2 adj	0.988	0.977	0.969
	χ^2	0.061	0.147	0.221
Freunlich	k_f (mg g^{-1})	0.154	3.430	4.658
	n	0.172	2.674	3.063
	R^2	0.982	0.976	0.956
	R^2 adj	0.980	0.972	0.950
	χ^2	0.107	0.178	0.356
D-R	$Q_{\max}$ (mg g^{-1})	5.953	6.841	6.908
	k ($\text{mol}^2 \text{J}^{-2}$)	$4 \text{ E} - 7$	$2 \text{ E} - 7$	$5 \text{ E} - 8$
	E (kJ mol^{-1})	1.118	1.581	3.162
	R^2	0.915	0.911	0.931
	R^2 adj	0.915	0.898	0.921
	χ^2	0.460	0.667	0.563

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