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Removal by adsorption of the drug tetracycline hydrochloride using bentonite clay mineral: Kinetic and isotherm evaluation

Aisha Victória Silva Pereira[a] , Adriano Magalhães Nunes Freitasa[a,b] , Heloise Oliveira Medeiros de Araújo Moura[a] , Enrique Rodríguez-Castellón [c], Luciene Santos de Carvalho [a,b,*]

[a] *Energy Technologies Laboratory LABTEN/UFRN, Rua das Humanidades, Natal - 59075-000, Brazil*
[b]*Post-Graduate Chemistry Program (PPGQ/UFRN), Natal - 59075-000, Brazil*
[c]*Dpto. de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga, Spain.*

Abstract

Bentonite (BN) is a clay mineral with broad industrial applications due to its swelling capacity, facilitating the adsorption of various molecules. Its use as an adsorbent for the removal of pharmaceuticals in aqueous media, such as tetracycline, is efficient, non-toxic, and low-cost, proving to be economically and environmentally viable. In this study, both natural and acid-treated bentonite (BN and BA1, respectively) were characterized using techniques such as X-ray fluorescence and diffraction (XRF and XRD), scanning and transmission electron microscopies (SEM and TEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TG/DTG). N2 adsorption/desorption analysis indicated that the clay mineral is mesoporous, with a surface area greater than 165 m².g-1 for BA1. The concentration of adsorbates was determined by UV-Vis spectrophotometry. The pseudo-second-order kinetic model ($R^2 = 0.9999$) fit all adsorbates, thus suggesting a chemisorption mechanism. The maximum adsorption capacity of tetracycline calculated by the Freundlich isotherm ($R^2 = 0.9873$) was 30.39 mg.g-1 for BA1, with approximately 97% (BN) and 99% (BA1) removal within 30 minutes using 0.3 g of adsorbent and an initial concentration of 300 mg.L-1 . Bentonite demonstrated high efficiency as adsorbent for tetracycline hydrochloride, standing out as a natural, low-cost, and environmentally friendly material.

Keywords: Bentonite; Adsorption; Water treatment; Environmental remediation; Tetracycline

1. Introduction

The inclusion of pharmaceutical residues in the category of Contaminants of Emerging Concern (CECs) is a result of the increased concentration of these substances in aquatic effluents [1]. This scenario has encouraged the research of new adsorbent materials that offer more effective removal of these compounds and cause less environmental impact. Among antibiotics, tetracycline hydrochloride is one of the most consumed globally due to its high antimicrobial activity and low cost, and it is widely used in the animal industry and aquaculture. This antibiotic, which has functional groups such as alcohol, phenol, enol, amide, ketone, and amino, is highly recalcitrant and is often found in aquatic environments. It can be solubilized in acidic and basic media, in the presence of nonpolar organic solvents and alcohols [2]. Its absorption rate is low in animals, even with high dosages, resulting in 50% to 80% of the medication being released in the environment by excretion, which contributes to the increase of antibiotic-resistant bacteria [3]. To resolve these problems, various wastewater treatment methods are studied in the literature, including membrane separation, oxidative degradation, electrochemical degradation, adsorption, and photodegradation [4]. Adsorption is a popular method due to its low cost, efficiency, and ease of implementation. The use of natural adsorbents, such as clay minerals, has shown promising results in recent years [5]. Studies indicate that acid-treated modified bentonite provides better contaminant removal due to the increased contact area resulting from the leaching of some metals present on the material's surface [6,7]. Bentonite is a clay mineral primarily composed of montmorillonite, a hydrated aluminum silicate with structural formula $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. Belonging to the smectite group, bentonite has a structure composed of layers of silica tetrahedrons and aluminum octahedrons. These layers are separated by a layer of water and exchangeable cations, which gives bentonite

its swelling capacity and high specific surface area. Studies of its applications are widely disseminated in various research fields, being used both in its natural and modified forms. In this context, this work proposes an alternative method to mitigate tetracycline hydrochloride contamination in aqueous effluents, using the widely abundant clay mineral bentonite as adsorbent, with a low-cost method economic, energy, and environmental.

2. Experimental

2.1 Modification of bentonite

The methodology employed in this study involved using bentonite in its natural form (BN) and after acid modification (BA1). For the modification process, hydrochloric acid (HCl 37%) with concentrations of 1 and 2.5 mol.L^{-1} was applied to treat the clay mineral. The acidic solution was added to BN and stirred continuously at 60 °C for 4 hours. Following the acid treatment, the material underwent vacuum filtration and washing to separate the solid from the liquid and to neutralize the pH. The samples were then dried in an oven at 80 °C for 12 hours, resulting in the samples being designated as BA1 and BA2.5, respectively. Based on preliminary tests, only BA1 was selected for further use. The samples after adsorption were labeled BNF and BA1F.

2.2 Adsorption of tetracycline hydrochloride

2.2.1 Kinetics of tetracycline drug adsorption

The rate of tetracycline adsorption was examined over a period ranging from 1 minute to 24 hours, with continuous stirring at 150 rpm on a shaking table (SL - 180/DT - SOLAB). In the kinetic experiments, 25 mL of tetracycline solutions at 500 ppm and 0.3 g of the adsorbents were placed in Erlenmeyer flasks. The adsorption capacity of the adsorbents was then calculated using pseudo-firstorder, pseudo second-order, and Elovich kinetic models, which were fitted using Excel and Origin 2019b software.

2.2.3 Equilibrium of tetracycline drug adsorption. Adsorption isotherms were obtained for concentrations ranging from 25 to 500 mg.g-1 of tetracycline. For this, 250 mL Erlenmeyer flasks containing 0.3 g of either natural or acid-treated bentonite and 25 mL of the solution were stirred at 150 rpm for 30 minutes. The solutions were then centrifuged at 3000 rpm for 20 minutes to separate the solid and liquid phases. The adsorption equilibrium was analyzed using four isotherm models: Langmuir, Freundlich, SIPS, and Temkin.

2.2.1 Drug quantification

The concentration of tetracycline hydrochloride in the solution, initially set at 500 ppm, was measured after the adsorption tests using a UV-Vis spectrophotometer (Shimadzu 1800) at a wavelength of 360 nm to determine the final concentration.

3. Results

3.1 Adsorption kinetics

Comparing the clay mineral before and after treatment, BA1 showed the highest experimental adsorption capacity (qe = 41.35 mg.g^{-1}). The adsorption study with BN modified with 1 mol.L-1 HCl (qe = 40.98 mg.g^{-1}) showed an increase in the amount of drug adsorbed compared to BN (qe = 40.60 mg.g-1) (Table 1), demonstrating the effectiveness of acid treatment in improving the tetracycline adsorption process. Among the three models studied, the pseudo-second-order model best fit the data, with a determination coefficient close to 1 (R^2 = 0.999). Additionally, this model showed a small difference between the experimental (41.35 mg.g^{-1}) and calculated (40.60 mg.g^{-1}) qe values, suggesting that chemisorption is the rate-determining step in the tetracycline adsorption process, involving an electron exchange or sharing mechanism between the adsorbent and adsorbate [8].

Table 1. Kinetic parameters of adsorption

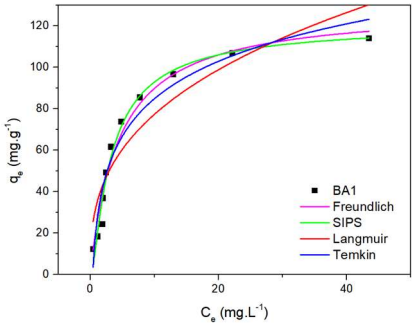
Kinetics parameters	BN	BA1
$q_{e,exp}$ (mg.g^{-1})	40,60	41,35
Pseudo-firts order		
k_1 (min^{-1})	-0,0008	0,0005
$q_{e,cal}$ (mg.g^{-1})	0,2716	1,7124
R^2	0,7004	0,1442
Pseudo-second order		
k_2 (g.mg^{-1}.min^{-1})	0,2421	-0,1804
$q_{e,cal}$ (mg/g)	40,65	41,00
R^2	0,9999	0,9999
Elovich		
α (mg.g^{-1} min^{-1})	$7,30x10^{-2}$	$3,9x10^{-18}$
β (g.mg^{-1})	0,309	0,539
R^2	0,0103	0,0355

3.2 Adsorption isotherms

The parameters of the models used are presented in Figure 1. The equilibrium isotherm calculations showed a better fit to the Freundlich model (R^2 > 0.9899), indicating that the predominant mechanism is physisorption and suggesting that the adsorption process involves the formation of multilayers on the adsorbent surface. The (K_F=34.1676) value demonstrates that the adsorption of tetracycline is favorable, as it is related to the material's adsorption capacity, indicating a high affinity for the adsorbate. In the case of the Langmuir model (R^2 = 0.9679), the results point to the formation of a monolayer on the

adsorbent surface, with a finite number of adsorption sites (Langmuir, 1916). The range ($0<R_L<1$) also confirms that the tetracycline adsorption process is favorable. Furthermore, the fit to the Temkin model ($R^2 > 0.9383$) suggests a linear decrease in the adsorption heat of the adsorbate molecules as the adsorbent surface becomes covered and indicates a maximum distribution of adsorption energy [11].

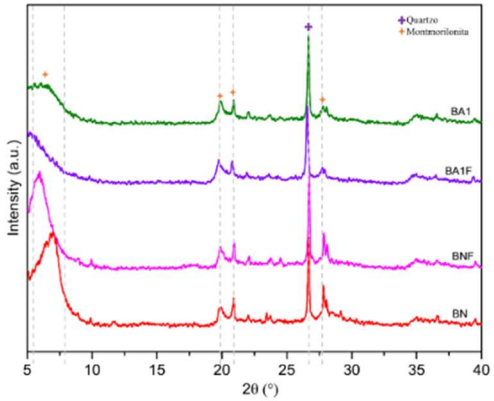
Fig. 1. Equilibrium parameters of adsorption



3.3 X-ray diffraction (XRD)

The XRD of this studied clay is very characteristic due to the peaks found for montmorillonite, quartz, and feldspar. The XRD pattern of natural sodium bentonite is shown in Figure 2 and demonstrates that the clay is predominantly composed of montmorillonite, with characteristics at d_{001} = 14.29 Å and d_{020} = 4.49 Å. The basal spacing of d_{001} = 14.29 Å suggests a predominance of sodium, allowing the classification of the samples primarily as sodium bentonite (Na-bentonite). Other observed peaks correspond to impurities of quartz and feldspar, commonly found in this clay [9].

Fig. 2 XRD patterns for bentonite samples.



3.4 N_2 adsorption-desorption isotherms

N_2 adsorption-desorption isotherms at 77 K for the BN, BNF, BA1, and BA1F samples are depicted in Figure 3. According to the IUPAC classification, these isotherms are type IV with H2 hysteresis loops, suggesting characteristics of mesoporous materials. The acid treatment appears to have increased the specific surface area (BET) by opening structural channels during leaching, which dissolved octahedral cations on the adsorbent surfaces. These findings are summarized in Table 2 [10].

Fig. 3. N_2 adsorption-desorption isotherms of samples BN, BNF, BA1 and BA1F.

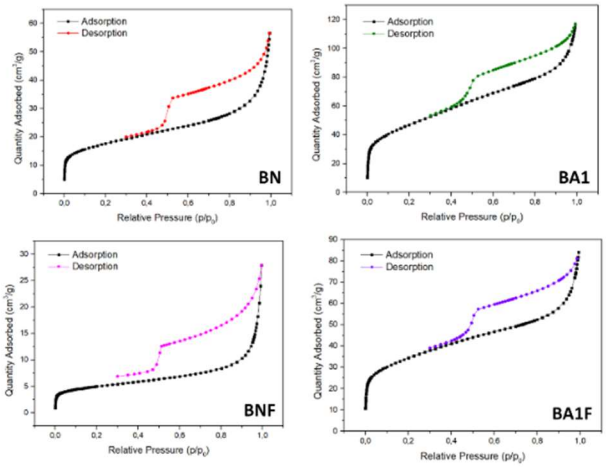


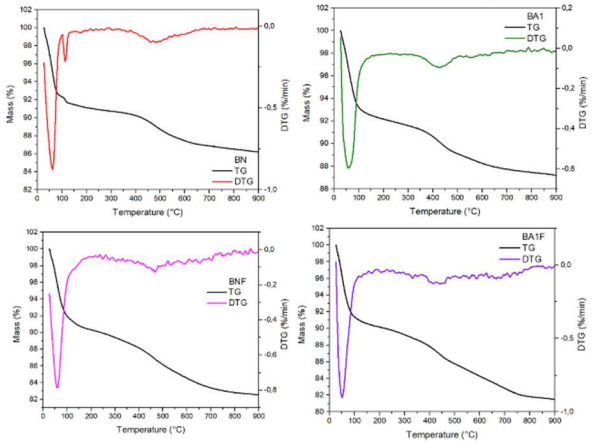
Table 2. N_2 adsorption-desorption isotherms data.

Samples	S_{BET}[a] ($m_2.g^{-1}$)	V_p[a] ($cm^3.g^{-1}$)	Pore Diameter (Å)
BN	62,83	0,06	37,43
BA1	165,43	0,15	35,29
BNF	17,78	0,02	43,78
BA1F	121,29	0,09	32,67

3.5 Thermogravimetric analysis (TG/DTG)

Thermogravimetric curves for the BN, BA1, BNF, and BA1F samples are shown in Figure 4. The first mass loss step occurs between 25 and 150 °C, associated with the water adsorbed on the external surface and between the interlamellar layers of bentonite [11]. There was no difference on the thermal degradation behavior of natural and modified bentonite samples at this stage, as both underwent a thermal pre-treatment at 80 °C. The second mass loss step represents the dihydroxylation of the clay mineral structures between 420 and 570 °C [12].

Fig. 4. TG/DTG curves for bentonite samples.



4. Conclusion

In this study, bentonite clay mineral emerges as a promising adsorbent for the removal of contaminants from water and pharmaceutical industry effluents. Aligning with the Sustainable Development Goals (SDGs, Agenda 2030), particularly Goal 12 – Responsible Consumption and Production, certain characterizations and applications were not conducted for the BA2.5 adsorbent. This approach reduces reagent consumption and waste, as BA1 demonstrated higher efficiency in removing the contaminant (tetracycline hydrochloride). The equilibrium isotherm calculations demonstrated the best fit to the Freundlich model (R^2 = 0.9873), indicating a physisorption mechanism. This suggests a heterogeneous system and an adsorption process involving the formation of a multilayer on the adsorbent surface. The bentonite clay mineral was also applied as an adsorbent for removing the antibiotic tetracycline from aqueous solutions. According to the kinetic data analysis, BA1 is optimally used with a contact time of 30 minutes and 0.30 g of adsorbent. Thus, bentonite stands out as an environmentally friendly and abundant material for application in the textile and pharmaceutical industries.

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