ADSORPTION OF TETRACYCLINE HYDROCHLORIDE USING BENTONITE CLAY: KINETIC AND EQUILIBRIUM EVALUATION

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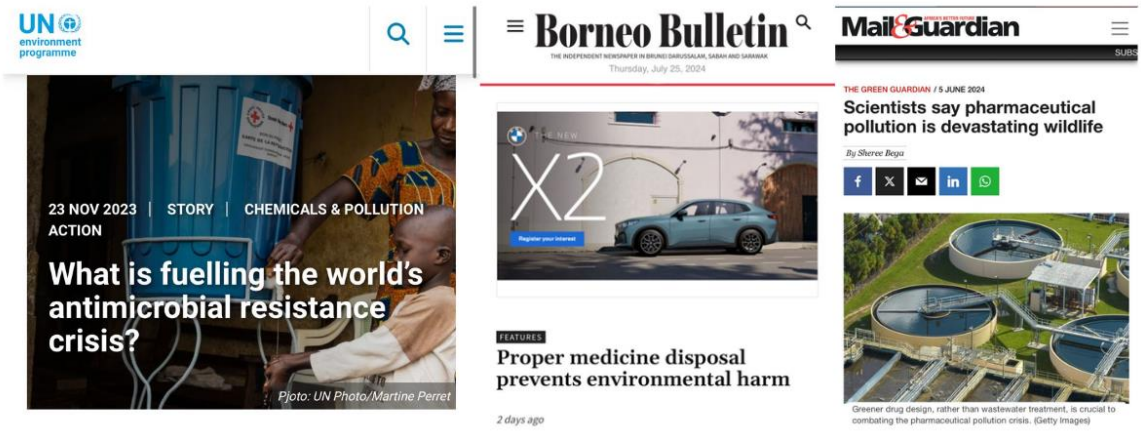
Palavras-Chave: Water treatment; Environmental remediation; Clay Mineral.

Introdução

The inclusion of pharmaceutical residues in the category of Contaminants of Emerging Concern (CECs) is a result of the increasing concentration of these substances in aquatic effluents (Farto et al., 2021). This situation has spurred research into new adsorbent materials that offer more effective removal of these compounds and cause less environmental impact. In addition to the issues shown in Figure 1, in 2021, the pharmaceutical market in Brazil generated R$20 billion, with most purchases occurring without a medical prescription, especially for medications for headaches, fever, and indigestion (Leite, 2022). According to the Federal Pharmacy Council (CFF), annually, 14,000 tons of expired medications are improperly disposed of (Regitano, 2010). These pharmaceutical residues are frequently detected in groundwater, sewage treatment plants, and water supply systems, highlighting the inefficacy of conventional methods used in water treatment plants (WTPs) to remove them (Fernandez, 2015).

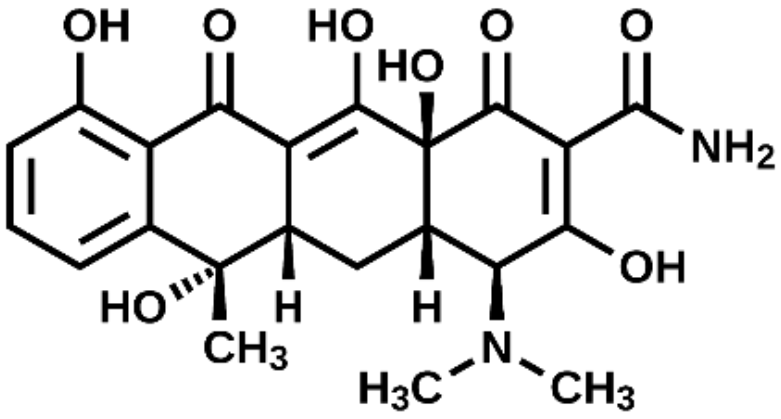
Figure 1. Problems with pharmaceutical contamination in Brazilian effluents.



Source: Environment Programme, Borneo Bulletin and The Green Guardian.

Among antibiotics, tetracycline hydrochloride, with its molecular structure shown in Figure 2, is one of the most widely consumed antibiotics globally due to its high antimicrobial activity and low cost, and it is widely used in the animal industry and aquaculture. This antibiotic, which contains functional groups such as alcohol, phenol, enol, amide, ketone, and amino, has high degradation resistance due to its recalcitrant nature and is frequently found in aquatic environments. It can be solubilized in acidic and basic media, in the presence of nonpolar organic solvents, and alcohols (Maia et al., 2009). The absorption rate is low in animals, even with high dosages, resulting in 50% to 80% of the drug meeting the environment, contributing to the increase of bacteria resistant to these antibiotics (Shi et al., 2024).

Figure 2. Molecular structure of the drug Tetracycline Hydrochloride



Source: Author, 2024.

Bentonite is a clay mineral primarily composed of montmorillonite, a hydrated aluminum silicate with structural formula $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$, as shown in Figure 3. 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 method with low economic, energy, and environmental cost.

In this context, the modification of bentonite emerges as a promising approach for the removal of emerging pharmaceutical contaminants, such as tetracycline hydrochloride, from aqueous effluents. Modification through acid treatments can significantly enhance the adsorbent's adsorption capacity, improving the effective removal of these compounds. This work aims to associate the characteristics of bentonite, such as high surface area and cation exchange capacity, with modifications that enhance its adsorption properties, to develop methodologies that not only improve the efficiency of antibiotic removal in water treatment plants but also minimize the environmental impact associated with the improper disposal of pharmaceutical residues.

Material e Métodos

The study involved the modification of natural bentonite (BN) through acid treatment with hydrochloric acid (HCl) at concentrations of 1 and 2.5 $mol.L^{-1}$, creating the samples BA1 and BA2.5. After stirring at 60 °C for 4 hours, the samples were filtered, washed, neutralized, and dried at 70 °C for 12 hours. Only the BA1 sample was used in subsequent tests.

The bentonite was characterized using various techniques, including X-ray diffraction (XRD), X-ray fluorescence (XRF), thermogravimetric analysis (TG), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS), high-resolution transmission electron microscopy (HRTEM), and X-ray photoelectron spectroscopy (XPS). These analyses allowed for the

evaluation of the crystalline structure, morphology, and chemical composition of the bentonite before and after modification.

The adsorption capacity of the modified bentonite was evaluated through isotherm and adsorption kinetics studies. Models such as Langmuir, Freundlich, Temkin, and Sips were tested to determine equilibrium behavior. The adsorption kinetics were studied using pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich models to understand the removal of tetracycline from aqueous solutions.

Specifically, for tetracycline, adsorption was studied over time intervals ranging from 1 minute to 24 hours, using 25 mL of tetracycline solution (500 ppm) and 0.3 g of adsorbents. The pseudo first-order, pseudo second-order, and Elovich kinetic models were fitted to the experimental data. Adsorption was conducted at various tetracycline concentrations (25 to 500 $mg.g^{-1}$) and at different temperatures (25 °C, 35 °C, and 45 °C), allowing for the determination of thermodynamic parameters ΔG°, ΔH°, and ΔS°, which describe changes in the system during the adsorption process.

The influence of pH on tetracycline adsorption was investigated at pH levels of 2.5, 4.5, 6.5, and 8.5, using 0.1 $mol.L^{-1}$ buffer solutions. After the experiments, the final concentration of tetracycline was determined by UV-Vis spectrophotometry at 360 nm.

This study provides a comprehensive understanding of the properties of modified bentonite and its potential as an adsorbent for the removal of pharmaceuticals like tetracycline from aqueous effluents.

Resultados e Discussão

Adsorption Isotherms

The parameters of the models used are presented in Table 1. The equilibrium isotherm calculations indicated a better fit to the Freundlich model ($R^2 > 0.9873$), suggesting a favorable adsorption process in heterogeneous systems or multilayer adsorption. Additionally, the values of $1 < n < 10$ confirm the favorability of the adsorption process of the drug under study (Freundlich, 1906). A fit to the Temkin model was also observed ($R^2 > 0.9163$), suggesting that a linear decrease in the heat of adsorption of the adsorbate molecules occurs as the adsorbent surface is covered, and it also indicates that the process presents a maximum distribution of adsorption energy (Sales, 2015; Silva, 2024). The results for the Langmuir model ($R^2 > 0.5722$) suggest that the adsorption process occurs with the formation of a monolayer on the surface of the adsorbent (Langmuir, 1916). The data obtained with the SIPS mathematical model did not yield good results.

Table 1. Adsorption isotherms of BN and BA1 samples.

Isothem Parameters	BN	BA1
Langmuir		
q_m (mg/g)	7,910	767454,8
$K_L \times 10^3$ (L/mg)	-9,2803	-3,5401
R_L	5,67E-6	1,033E-5
R^2	0,5423	0,5722
Freundlich		
N	0,2864	0,3112
K_F (L/g)	0,0088	0,6821
R^2	0, 9798	0, 9873
Temkin		
B ($J.mol^{-1}$)	20,8881	45,1889
b	4,4965	4,6181
K_t ($L.g^{-1}$)	0,1655	0,6547
R^2	0,7611	0,9164

Source: Author, 2024.

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 2), 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 (Silva, 2024). The Elovich equation was also applied and showed a poor fit for BA1 with $R^2 > 0.6831$, indicating that the regression model does not explain the data variability well (Eldoma, 2023).

Table 2. Kinetic parameters of BN and BA1 samples.

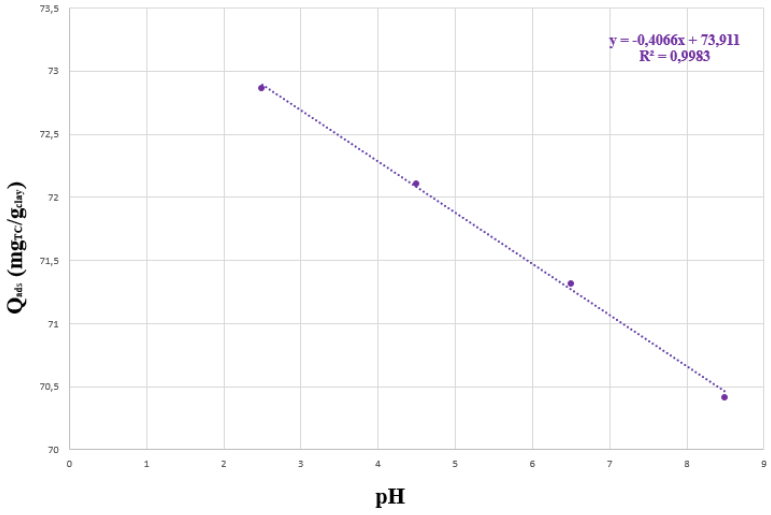
Kinetics parameters	BN	BA1
$q_{e,exp}$ (mg.g^{-1})	40,60	41,35
Pseudo-firts order		
k_1 (min^{-1})	-0,0008	0,0005
$q_{e,cal}$ (mg.g^{-1})	0,2716	1,7124
R^2	0,3795	0,1442
Pseudo-second order		
k_2 (g.mg^{-1}.min^{-1})	0,2421	-0,1804
$q_{e,cal}$ (mg/g)	40,65	40,98
R^2	0,9999	0,9999
Elovich		
α (mg.g^{-1} min^{-1})	7,30x10^{-2}	3,9x10^{-18}
β (g.mg^{-1})	0,309	0,539
R^2	0,4331	0,6831

Source: Author, 2024.

Influence of pH

The results presented in Figure 4 show that natural bentonite exhibits high TC adsorption at pH 2.5, which progressively decreases as the pH increases. These results are consistent with previous studies that reported the adsorption of tetracycline on natural clays (Fernandez, 2015). At acidic pH, the adsorption of TC on natural clay is primarily controlled by electrostatic interactions, with cation exchange being the dominant mechanism. However, as the medium's pH increases and TC species with lower affinity appear, adsorption may occur through other mechanisms, such as hydrogen bonding, hydrophobic interactions, or complex formation with surface groups of the clay mineral (Parolo et al., 2008).

Figure 4. Influence of pH on tetracycline adsorption with BN.

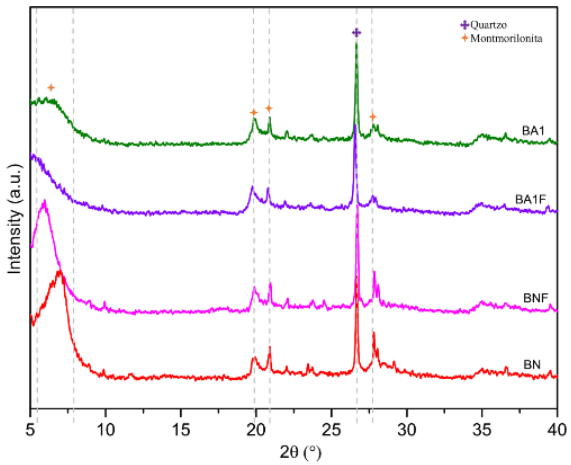


Source: Author, 2024.

X-ray Diffraction

Figure 5 shows the XRD pattern of natural calcium bentonite. As shown, the clay is predominantly composed of montmorillonite, with characteristics at d001 = 14.29 Å and d020 = 4.49 Å. The basal spacing of d001 = 39.8 Å suggests a predominance of calcium, allowing the samples to be classified primarily as calcium bentonite (Ca-bentonite) (Pokharel, 2021). After acid treatment, the X-ray diffraction pattern of activated bentonite shows a broadening of the peaks and increased intensity, indicating that the layered structure of bentonite was partially destroyed by the treatment, also affecting the adsorbent's crystallinity. This effect suggests deformation of the crystalline structure. The increase in the quartz peak, observed at 2θ around 26° after acid activation, reveals that the quartz present as an impurity was not destroyed during the activation process, and its intensity increases as the bentonite structure disintegrates (Bharali, 2024).

Figure 5. XRD of the samples

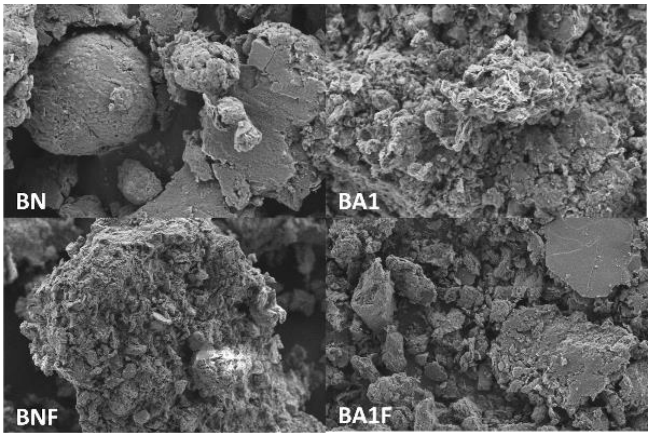


Source: Author, 2024

Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM/EDS)

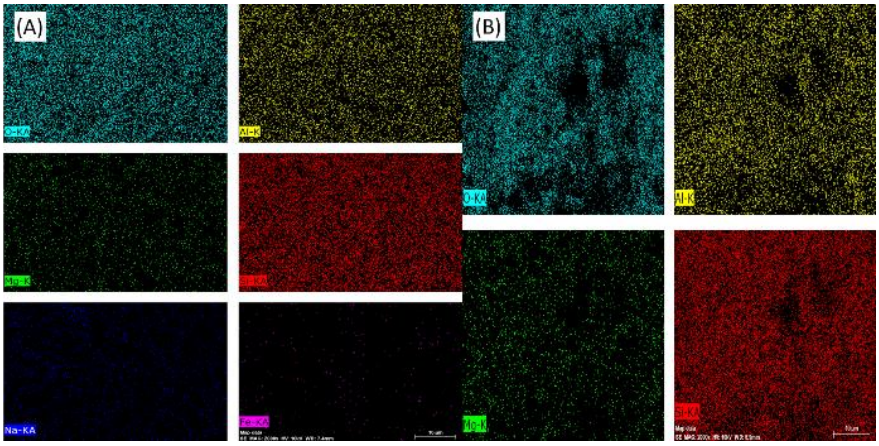
As reported in other studies in the literature (Rianna et al., 2024), bentonite exhibits amorphous characteristics due to its unclear morphology at the nanometric scale. The particle sizes vary for each sample due to differences in the treatment of each composition. The SEM-EDX images show some agglomerations in each sample, which may be influenced by the particle size of each sample as shown in Figure 6. The images (Figure 7) from the mappings obtained through EDS analysis confirm the presence and dispersion of the atomic components of the clay minerals on the surfaces of the materials.

Figure 6. SEM images of BN, BA1, BNF, and BA1F samples



Source: Author, 2024.

Figure 7. EDS Mapping of samples BN (A) and BA1 (B)

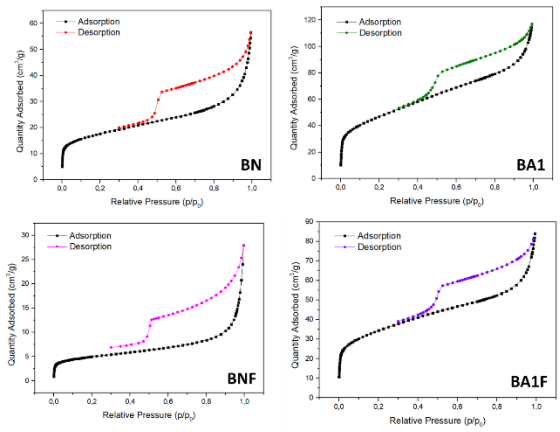


Source: Author, 2024.

N_2 Isotherm

The N_2 adsorption-desorption isotherms at 77 K for BN, BNF, BA1, and BA1F samples are shown in Figure 8. According to IUPAC classification, these isotherms are of type IV with H2 hysteresis loops, with $P/P_0 > 0.9$. In the low P/P_0 region ($P/P_0 < 0.1$), all samples exhibited a small amount of N2 adsorption, suggesting that there is almost no microporosity in the acid-activated clays. On the other hand, N_2 adsorption increases significantly in the high P/P_0 region, indicating the presence of mesopores in these clays (Zhong et al, 2024). Acid treatment increased the specific surface area (BET), as shown in Table 3, opening structural channels during leaching, which dissolved octahedral cations on the adsorbent surfaces. These results are summarized in Table 3 (Barrera et al, 2010).

Figure 8. N_2 adsorption isotherms of BN, BNF, BA1, and BA1F samples.



Source: Author, 2024.

Table 3. N_2 adsorption data of the samples.

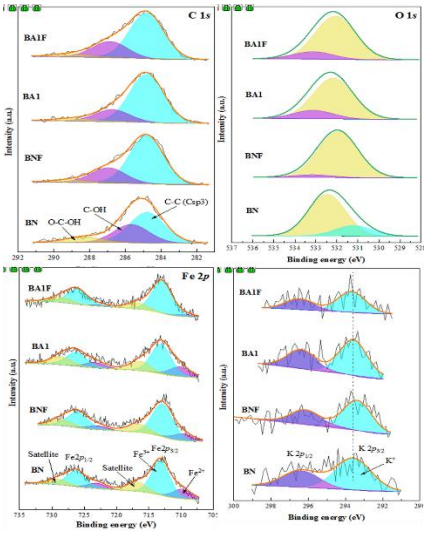
Samples	$S_{BET}{}^{a}$ ($m^2.g^{-1}$)	$V_p{}^{a}$ ($cm^3.g^{-1}$)	Pore Diameter (Å)
BN	62.83	0.06	37.43
BA1	165.43	0.15	35.29
BNF	17.78	0.02	43.78
BA1F	121.29	0.09	32.67

Source: Author, 2024.

X-ray Photoelectron Spectroscopy

The deconvolution of XPS spectra shown in Figure 9, is closely linked to their capacity to adsorb tetracycline. The adsorption of tetracycline is significantly influenced by the interactions between functional groups on the adsorbents and the antibiotic molecules. In the C 1s spectra, BA1F, BA1, and BNF materials exhibit C–C/C–H (Csp^3) and oxygenated groups, such as C–OH and O–C=O, which are crucial for tetracycline adsorption. These groups interact with tetracycline's amino and oxygenated functionalities through hydrophobic interactions, hydrogen bonds, and Van der Waals forces, potentially enhancing the adsorption capacity of these materials (Huang et al., 2023). Analysis of the O 1s spectra reveals that all materials contain oxygen bonded to carbonyl groups (C=O) and hydroxyls (C–O), which are also vital for adsorption, as they can form hydrogen bonds with tetracycline. BN with higher intensity in oxygen peaks, shows stronger interactions with tetracycline, leading to more efficient adsorption (Liu et al., 2017; Moura, 2023). The presence of iron oxides, particularly Fe^{2+} and Fe^{3+} in BA1F, BA1, and BNF materials, is another key factor. These iron species can coordinate with tetracycline's functional groups, increasing the materials' affinity for the antibiotic and suggesting additional active sites for adsorption (Sudan et al., 2024; Sales, 2015). The K 2p spectra analysis indicates the presence of potassium on the surfaces of the materials, especially in BN. (Silva, 2024).

Figure 9. Deconvolution of the XPS spectrum of the elements present on the surface of the samples.



Source: Author, 2024.

Conclusões

The clay mineral bentonite is presented in this study as a promising adsorbent for removing contaminants from pharmaceutical industry wastewater. In line with the Sustainable Development Goals (SDGs, Agenda 2030), particularly Goal 12, some characterizations and applications were not performed for the BA2.5 adsorbent, thereby reducing reagent use and waste generation in the study. This material, both in its natural form and after acid treatment, was characterized using various chemical techniques, such as XPS and EDS, revealing a composition rich in silicon and aluminum. SEM analysis indicated that bentonite organizes into aggregates with high amorphousness, showing little clarity on a nanometric scale. Additionally, acid treatment caused the leaching of surface impurities from the adsorbent, resulting in a significant increase in surface area. The chemical composition of the surfaces of the materials, as evidenced by XPS spectra, plays a crucial role in tetracycline adsorption. The BA1F, BA1, and BNF materials, with higher presence of oxygenated groups and iron in different oxidation states, likely exhibit greater adsorption capacity due to favorable chemical interactions. The BN material, with its higher surface oxidation and potassium presence, may show distinct adsorption behavior, influenced by variables such as pH and its ability to form hydrogen bonds with tetracycline. According to the results obtained from kinetic studies, the optimal condition for using BA1 was a contact time of 30 minutes and 0.30 g of adsorbent. The fit to the pseudo second-order kinetic model and the Freundlich isotherm suggests that the adsorption process involves both chemisorption and physisorption, indicating chemical and physical interactions between the adsorbent and the adsorbate. Detailed understanding of the chemical interactions involved helps in the development of more efficient and specific adsorbents for environmental and industrial applications.

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