

Article

Efficient Removal of Tetracycline Hydrochloride via Adsorption onto Modified Bentonite: Kinetics and Equilibrium Studies

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Featured Application: This study provides insights for the development of efficient wastewater treatment systems targeting the removal of pharmaceutical pollutants, particularly tetracycline hydrochloride. The findings can be applied to advanced adsorption processes using modified bentonite, contributing to environmental sustainability and public health protection.

Abstract: Pharmaceutical contamination of water sources has become a critical environmental challenge. Bentonite (BN), a natural clay mineral, has gained attention due to its high surface area, cation exchange capacity, and cost-effectiveness, making it a promising adsorbent for removing contaminants. This study explores the potential of BN and its acid-treated form (BA1) as effective adsorbents for the removal of tetracycline hydrochloride (TC) from aqueous solutions. Comprehensive characterization was performed using analytical techniques, including XRF, XRD, SEM/TEM, XPS, TG/DTG, and CO₂ and N₂ adsorption–desorption isotherms. The results indicate that BA1 is a mesoporous material with a surface area exceeding 165 m²·g^{−1}. The adsorption process was fitted to a pseudo-second-order kinetic model. BA1 achieved a maximum adsorption capacity of 40.98 mg·g^{−1} and removal efficiency of up to 99% within only 30 min at an optimal pH of 5. Equilibrium isotherm calculations for BA1 show the best fit for the Freundlich model $R^2 > 0.9923$, indicating a favorable adsorption process. The material was reused over seven consecutive cycles to evaluate the regeneration capacity of the clay mineral materials. BN stands out for its effectiveness, cost-effectiveness, and environmental sustainability as a promising material for water treatment applications.

Keywords: tetracycline hydrochloride; bentonite; environmental remediation; drug adsorption; contaminant removal



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1. Introduction

Water contamination by pharmaceutical residues has been widely recognized as an emerging environmental issue, necessitating effective solutions to mitigate its impacts. The increasing concentration of these substances in aquatic effluents has led to their classification as Contaminants of Emerging Concern (CECs) [1]. Among these contaminants, the residues of tetracycline hydrochloride (TC), an antibiotic known for its high persistence

and low biodegradability, are of particular concern. These properties allow for the accumulation of TC in aquatic environments, promoting the spread of antimicrobial resistance [1]. Additionally, the absorption rate in animals is low, even at high dosages, with 50% to 80% of the drug entering the environment, contributing significantly to the rise of bacteria resistant to these antibiotics [2]. In Brazil, the pharmaceutical industry reported revenues of approximately BRL 20 billion in 2021, which resulted in the improper disposal of significant volumes of medications. It is estimated that 14,000 tons of expired drugs are discarded annually, exacerbating the contamination of water bodies [3,4].

The inclusion of pharmaceutical waste in the class of Contaminants of Emerging Concern (CECs) has led to an increased demand for new methods to mitigate these pollutants while minimizing environmental impact. Most pharmaceuticals are not completely metabolized by the body and are excreted through urine and feces. Even in minimal concentrations, these substances have been shown to have harmful effects on biota and pose significant risks to public health. Conventional water treatment techniques, such as coagulation–flocculation, membrane filtration, electrochemical degradation, photodegradation, and advanced oxidation, have been studied to remove pharmaceutical residues but exhibit significant limitations, particularly because many of these compounds are recalcitrant in nature [5]. Additionally, these techniques often come with high operational costs and can generate potentially toxic byproducts, which reduce their economic and environmental feasibility on a large scale [6].

Among the various treatment options, adsorption has been extensively studied as a promising alternative due to its efficiency, simplicity, and low cost [7]. In particular, bentonite, a natural clay mineral, has gained attention for its favorable structural properties, such as high surface area and cation exchange capacity [8]. Bentonite is a clay mineral composed primarily of montmorillonite, a hydrated aluminum silicate with the structural formula $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$. Belonging to the smectite group, bentonite has a layered structure consisting of silica tetrahedral sheets and aluminum octahedral sheets. These layers are separated by an interlayer space filled with water molecules and exchangeable cations, which confer its swelling ability and high specific surface area.

When treated with acid, bentonite's adsorptive properties are further enhanced by increasing its porosity and removing surface impurities, making it more efficient in removing pharmaceutical contaminants [9]. The use of natural adsorbents like bentonite for the removal of drugs has demonstrated satisfactory results in recent years, highlighting the potential of such materials for sustainable water treatment. However, there is still a lack of comprehensive studies on the interaction mechanisms between modified bentonites and pharmaceuticals, as well as the feasibility of large-scale application. To address this gap, this study investigates the effectiveness of both natural (BN) and acid-treated (BA1) bentonite in removing TC from aqueous solutions. Advanced characterization techniques, such as X-ray fluorescence (XRF), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDS), were employed alongside adsorption isotherm studies to understand the mechanisms involved in this process. The results of this research will contribute to the development of more sustainable water treatment technologies, expanding the potential applications of bentonite in the remediation of pharmaceutical pollutants and reducing the ecological risks posed by contaminants like tetracycline and other pharmaceutical residues.

2. Materials and Methods

2.1. Modification of Bentonite

Bentonite was kindly donated by Vurgel (Uruguaiana, RS, Brazil) in its powder form (>100 mesh). In this study, natural bentonite (BN) was compared to its acid-modified form to evaluate adsorption performance. The modification process involved treating BN with hydrochloric acid (HCl, 37%, Neon). Preliminary tests indicated that bentonite material treated with 1 mol·L⁻¹ HCl (BA1) and 2.5 mol·L⁻¹ HCl (BA2.5) exhibited similar performance in TC adsorption. Therefore, the HCl solution with the lower acid concentration (1 mol·L⁻¹) was chosen for further evaluation, aligning with Principle 1 of Green Chemistry (atom economy). The acid solution was mixed with BN under continuous stirring at 60 °C for 4 h to enhance its adsorptive properties. Following the acid treatment, the material underwent vacuum filtration, and the solid was subsequently washed to a neutral pH. The treated material was then dried in an oven at 70 °C for 12 h to ensure complete removal of moisture. The resultant acid-modified bentonite sample was named BA1 and selected for subsequent adsorption studies based on its superior performance observed in preliminary evaluations.

2.2. Characterization of Bentonite Materials

The bentonite materials before (BN and BA1) and after drug adsorption (BNF and BA1F) were characterized by a set of instrumental techniques. X-ray diffraction (XRD) was performed with a Bruker D2 Phaser instrument (CuK α , λ = 1.54 Å, Madison, WI, USA), while their elemental composition was determined using X-ray fluorescence (XRF) with a Bruker S2 Ranger. Thermogravimetric analysis (TGA) was used to assess thermal stability and decomposition behavior, conducted on a NETZSCH TG 209 F3 Tarsus under a nitrogen atmosphere, with a heating rate of 5 °C·min⁻¹.

Morphological and elemental analysis was carried out by scanning electron microscopy (SEM) coupled to energy-dispersive X-ray spectroscopy (EDS) using a Carl Zeiss Auriga 40 instrument equipped with a Bruker XFlash 410-M detector. High-resolution transmission electron microscopy (HRTEM) was conducted with a TALOS F200x instrument, providing detailed imaging at 200 kV in scanning transmission electron microscopy (STEM) mode with a high-angle annular dark-field (HAADF) detector.

Surface area and pore structure were analyzed using nitrogen adsorption/desorption isotherms at −196 °C, with measurements taken using a Micromeritics ASAP 2420 system. X-ray photoelectron spectroscopy (XPS) was performed with a PHI 5700 spectrometer using non-monochromatic AlK α radiation (95.2 W, 15 kV, and 1486.6 eV) to examine surface chemistry and elemental composition.

2.3. Preparation of TC Solutions

To simulate a contaminated aqueous effluent, tetracycline hydrochloride (TC), (TETRAMED, Sao Paulo, Brazil) was selected as the model compound. A 500 mg·L⁻¹ solution of TC was initially prepared, and kinetic, equilibrium, and thermodynamic isotherm measurements were then conducted using an initial concentration of 25 mg·L⁻¹. After the adsorption tests, the remaining concentration of the drug was quantified by UV-Vis spectrophotometry (Shimadzu 1800, Kyoto, Japan) at a wavelength of 360 nm to determine the final TC concentration.

2.4. Adsorption Kinetics Studies

The adsorption mechanism of TC was investigated by evaluating the kinetic parameters over a range of contact times. For these experiments, 0.3 g of adsorbent was added to 25 mL of a 500 mg·L⁻¹ TC solution. The tests were conducted at 25 °C (room tem-

perature) under constant stirring at 150 rpm, with sampling intervals ranging from 1 to 1440 min (11 data points). Residual TC concentrations were quantified using UV-Vis spectrophotometry.

The adsorption capacity and kinetic behavior were analyzed by applying multiple kinetic models, including the pseudo-first-order, pseudo-second-order, and Elovich models, as described by Equations (1)–(3), respectively. Data fitting and model comparisons were performed using Excel and Origin 2019b software to identify the most suitable kinetic mechanism governing the adsorption process.

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

$$q_t = \frac{\ln (\alpha \beta)}{\beta} + \frac{1}{\beta} \ln t \quad (3)$$

In the kinetic models applied to analyze the adsorption process, q_t represents the amount of tetracycline hydrochloride adsorbed per gram of adsorbent at time t , while q_e denotes the adsorption capacity of the material at equilibrium, both expressed in $\text{mg} \cdot \text{g}^{-1}$. The pseudo-first-order rate constant, k_1 ($\text{L} \cdot \text{min}^{-1}$), characterizes the rate of adsorption as proportional to the difference between q_e and q_t . Similarly, the pseudo-second-order rate constant, k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$), reflects the chemisorption kinetics, which are often associated with valence forces or electron exchange. The parameter β ($\text{g} \cdot \text{mg}^{-1}$) is related to the activation energy for chemical adsorption and provides insights into the extent of surface coverage. Additionally, α ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$) represents the initial adsorption rate and describes the adsorption behavior as $t = 0$. These parameters, derived from fitting experimental data to the kinetic models, provide detailed insights into the adsorption dynamics and the mechanisms governing the process.

The Mean Squared Error (MSE) was used to evaluate the accuracy of the model in estimating the TC concentration after the adsorption process. The MSE is a widely used metric to quantify the difference between experimental and predicted values, calculated using Equation (4):

$$MSE = \frac{1}{n} \sum_{i=1}^n (C_{exp,i} - C_{pred,i})^2 \quad (4)$$

where $C_{exp,i}$ represents the experimental drug concentration at point i , $C_{pred,i}$ is the concentration predicted by the model, and n is the total number of observations. Lower MSE values indicate greater accuracy of the model in fitting the data.

2.5. Adsorption Equilibrium Study

The adsorption isotherms were determined using tetracycline hydrochloride solutions with concentrations ranging from 25 to 500 $\text{mg} \cdot \text{L}^{-1}$. For each experiment, 0.3 g of natural or acid-treated bentonite was added to 25 mL of the solution in 250 mL Erlenmeyer flasks. The mixtures were agitated at 150 rpm for 30 min to ensure interaction between the adsorbent and the adsorbate. After the adsorption process, the solid and liquid phases were separated via centrifugation at 3000 rpm for 20 min.

The experimental data were analyzed using non-linear forms of the Langmuir, Freundlich, Sips, and Temkin isotherm models, represented by Equations (5)–(8), respectively. These models were employed to describe the equilibrium behavior of tetracycline adsorp-

tion and evaluate the adsorption capacity and the nature of the interactions between the adsorbent and the adsorbate.

$$q_e = \frac{q_m * K_L * C_e}{1 + K_L * C_e} \quad (5)$$

$$q_e = K_F * C_e^{\frac{1}{n}} \quad (6)$$

$$q_e = \frac{q_m * K_s * C_e^{\frac{1}{n}}}{1 + K_s * C_e^{\frac{1}{n}}} \quad (7)$$

$$q_e = B * \ln K_T + B * \ln C_e \quad (8)$$

where C_e is the concentration ($\text{mg} \cdot \text{L}^{-1}$); q_e is the amount of adsorbed drug ($\text{mg} \cdot \text{g}^{-1}$); q_m is the maximum adsorption capacity; K_L , K_F , K_s and K_t are the Langmuir, Freundlich, Sips, and Temkin constants, respectively; n is the Sips coefficient; K_T is the binding constant at equilibrium, and B is the constant related to the heat of sorption ($B = \frac{RT}{b_t}$).

2.6. Influence of pH

To analyze the effect of pH on drug adsorption, 0.1 $\text{mol} \cdot \text{L}^{-1}$ buffer solutions were added to the adsorption systems to adjust the pH to 2.5, 4.5, 6.5, and 8.5, respectively. After the adsorption experiments, the final concentration of tetracycline was determined using a UV-Vis spectrophotometer (Shimadzu 1800, Kyoto, Japan) at a wavelength of 360 nm.

2.7. Reuse of the Adsorbent

After adsorption, the adsorbent was washed with deionized water until any traces of the non-adsorbed drug were removed. The material was then dried in an oven at 70 °C for 8 h. Finally, the adsorbent was treated with a 0.1 $\text{mol} \cdot \text{L}^{-1}$ HCl solution for 4 h at 50–60 °C under stirring, dried at 80 °C for 6 h, and then placed into a new TC solution system for another adsorption cycle. This process was conducted seven times to evaluate the reuse efficiency.

3. Results

3.1. Influence of pH in TC Adsorption by Bentonite Materials

The results presented in Figure 1 indicate that natural bentonite exhibits a high adsorption capacity for tetracycline (TC) at pH 2.5, with a progressive decrease in adsorption as pH increases. This trend is consistent with previous studies on tetracycline adsorption onto natural clays [9]. At low pH, the bentonite surface is predominantly protonated, acquiring a positive charge due to the adsorption of H^+ ions. Simultaneously, tetracycline is primarily present in its cationic form (TC^+), which enhances electrostatic interactions with the negatively charged sites on the clay. Under these conditions, cation exchange becomes the dominant adsorption mechanism, contributing to the high adsorption capacity observed at acidic pH. Additionally, the formation of hydrogen bonds between the protonated functional groups of TC and hydroxyl groups on the bentonite surface may further promote adsorption [2,10,11].

As pH increases, the surface charge of bentonite becomes less positive, and the ionization state of tetracycline changes. At intermediate pH values (4–7), TC predominantly exists in its zwitterionic form (TC^0), reducing electrostatic attractions with the clay surface and leading to a gradual decline in adsorption. At higher pH levels (above 7), tetracycline primarily exists in its anionic form (TC^-), while the bentonite surface acquires a net negative charge due to the deprotonation of hydroxyl groups [5,6]. This results

in electrostatic repulsion between the adsorbent and the adsorbate, further decreasing adsorption efficiency.

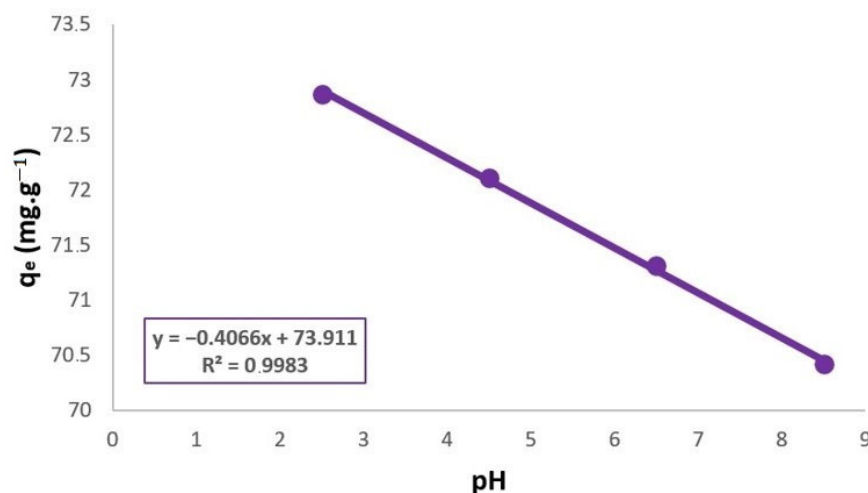


Figure 1. Influence of pH on tetracycline adsorption with BN.

The linear correlation observed between adsorption capacity (q_e) and pH, as indicated in Figure 1, suggests that pH-dependent electrostatic interactions play a dominant role in the adsorption process. However, secondary interactions, including van der Waals forces and surface complexation, may also influence the overall adsorption behavior [11–13].

3.2. Compositional Analysis by X-Ray Fluorescence Spectroscopy (XRF)

The inorganic elements present in natural bentonite (BN) and acid-treated bentonite (BA1) are listed in Table 1. Silicon (Si) was the predominant element in both samples, with a notable increase from 52.35% in BN to 62.51% in BA1. This increase is attributed to the removal of impurities and the dissolution of cations during acid treatment, which enriches the bentonite structure with silica [14]. Iron (Fe) content decreased from 18.57% to 13.13% after acidification, indicating the partial leaching of iron oxides from the structure. This leaching is associated with the removal of impurities, such as hematite and goethite, which are commonly found in natural bentonites [15]. Aluminum (Al) and silicon (Si) are the primary components of bentonite, with the high Al content expected due to its montmorillonite composition. Even after acid treatment, the Al content remained unchanged, demonstrating the stability of montmorillonite—the primary clay mineral in bentonite—and the preservation of its crystalline structure [14,15]. Cristobalite impurities are associated with silica (SiO₂) [9]. The concentrations of exchangeable cations, including potassium (K), calcium (Ca), sodium (Na), and magnesium (Mg), decreased following acid treatment. The calcium content declined from 2.73% to 1.23%, while sodium was completely removed (0.87% to 0.00%), confirming that the analyzed bentonite was predominantly calcium-type (Ca-bentonite). The extraction of these cations highlights the effect of acid treatment on ion exchange and the dissolution of secondary mineral phases, such as feldspars and carbonates [11].

Table 1. XRF results for BN and BA1 samples.

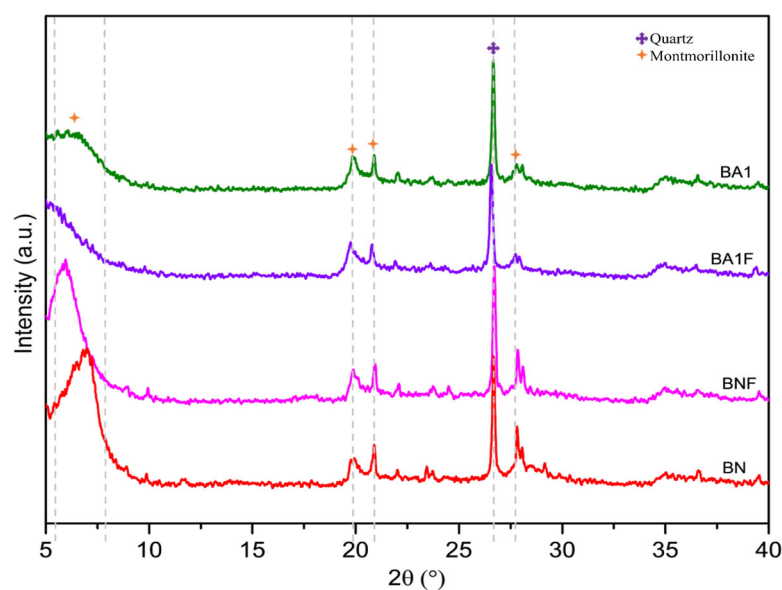
Element	BN—Composition (a%)	BA1—Composition (a%)
Si	52.35	62.51
Fe	18.57	13.13
Al	15.18	15.83
K	3.42	3.28
Ca	2.73	1.23

Table 1. *Cont.*

Element	BN—Composition (a%)	BA1—Composition (a%)
Na	0.87	0.00
Mg	2.06	1.93
Others	4.65	2.06

3.3. Structure and Morphology Assessment via XRD Patterns, SEM-EDS, and HRTEM Micrographs

XRD patterns for natural bentonite (BN), drug-loaded bentonite (BNF), modified bentonite (BA1), and drug-loaded modified bentonite (BA1F) are depicted in Figure 2. The diffractograms show characteristic peaks of montmorillonite along with impurities, such as quartz and feldspar. In BN, the characteristic montmorillonite peaks appear at approximately $5\text{--}10^\circ 2\theta$, corresponding to the basal plane $d_{001} = 14.29 \text{ \AA}$, confirming the presence of a smectitic structure with calcium intercalation. Additionally, a secondary peak at $4.49 \text{ \AA}$ (d_{020}) further supports the identification of montmorillonite as the dominant mineral. The d_{001} basal spacing of $39.8 \text{ \AA}$ confirms that the clay is classified as calcium bentonite (Ca-bentonite), as the presence of hydrated calcium cations directly influences the expansion of the crystalline layers [12].

**Figure 2.** XRD of samples BN, BNF, BA1, and BA1F.

The peak observed around $7^\circ (2\theta)$ shows significant variation among the samples, which can be attributed to structural modifications in the montmorillonite layers. This shift and intensity change likely results from interlayer expansion or contraction caused by acid treatment, leading to peak displacement [11,12]. The presence of quartz is evidenced by an intense peak at approximately $26^\circ 2\theta$, characteristic of the crystalline plane of SiO_2 . This peak appears in all samples, indicating that quartz persists even after chemical modifications. Smaller peaks associated with feldspar are observed in the range of $20\text{--}30^\circ 2\theta$, corresponding to common impurities in natural bentonites. After acid treatment (BA1), a broadening of the montmorillonite peaks is observed, suggesting a reduction in crystallinity and partial structural disorder due to cation dissolution and impurity removal. This effect is more pronounced in the shift of the d_{001} basal peak, indicating a contraction of the layered structure due to the extraction of interlayer ions [12].

SEM images for bentonite adsorbents (BN and BA1) and their respective drug-loaded samples (BNF and BA1F) are presented in Figure 3. As reported in other studies, bentonite

exhibits a certain degree of amorphicity due to its undefined morphology at the nanometric scale. The images show variations in particle size, influenced by the treatment and changes in sample composition. In the BN sample, larger and more defined particles are observed, with some spherical agglomerates, indicating a relatively intact clay structure. After acid treatment (BA1), the particles appear more fragmented and disordered, suggesting the removal of interlayer cations and partial dissolution of the clay mineral structure. These morphological changes align with the structural modifications observed in the XRD results, confirming the impact of acid activation and drug incorporation on the physicochemical properties of bentonite [13].

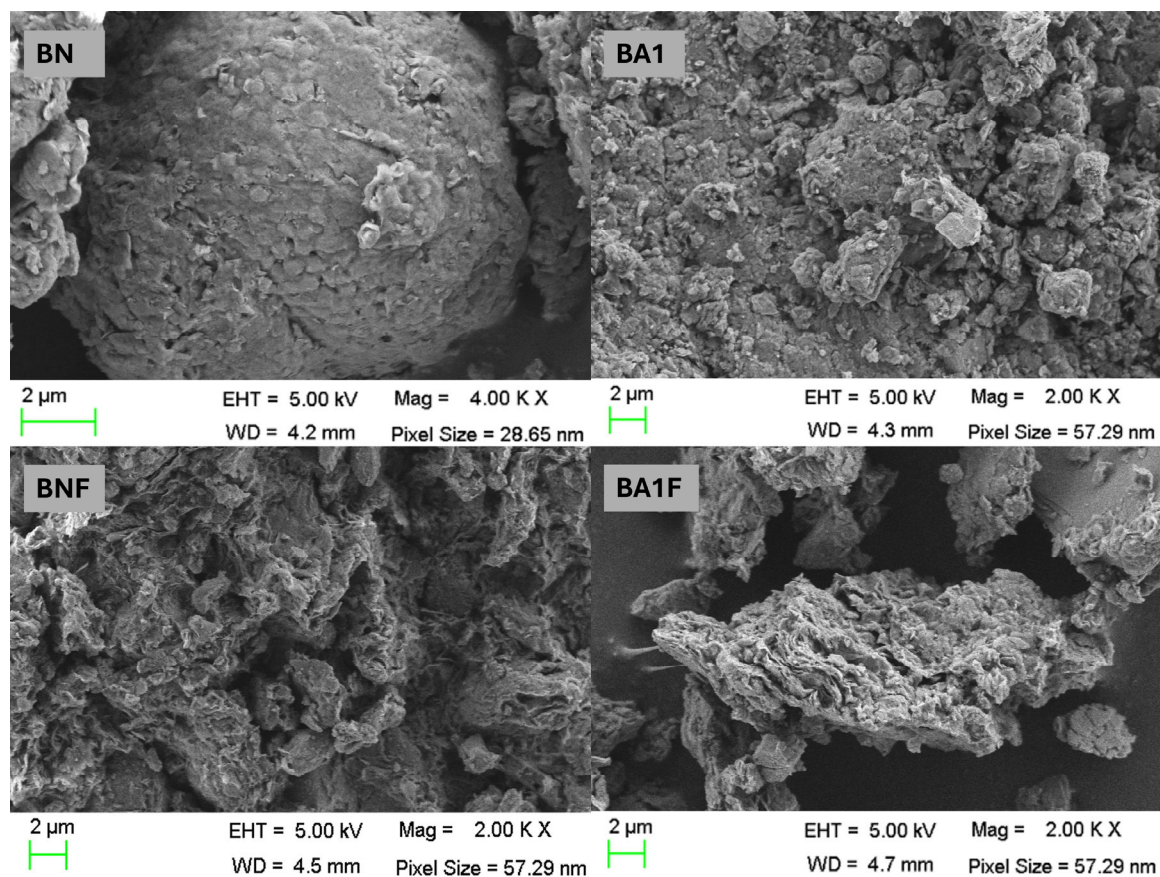


Figure 3. SEM images of BN, BA1, BNF, and BA1F samples. Scale bars indicate 2 μm.

TEM images (Figure 4) highlight significant morphological differences induced by the acid activation process. The BN sample exhibits relatively dense and layered structures with distinguishable plate-like particles, suggesting a well-preserved clay mineral framework. In contrast, the BA1 sample shows a more fragmented and amorphous appearance, with irregular and thinner layers, indicating partial dissolution of the clay structure due to acid leaching. These changes align with the XRD and SEM results, confirming the reduction in crystallinity and increased disorder after acid treatment. The presence of darker regions in the BA1 sample suggests the formation of defects and the removal of interlayer cations, contributing to the modified physicochemical properties of bentonite [14].

The data from the EDS mapping analysis (Figure 5) confirm the presence and dispersion of atomic components of the clay minerals on the surfaces of the materials. Similar to the results from the XRF analysis, the data indicate that the composition is primarily composed of aluminum and silicon atoms.

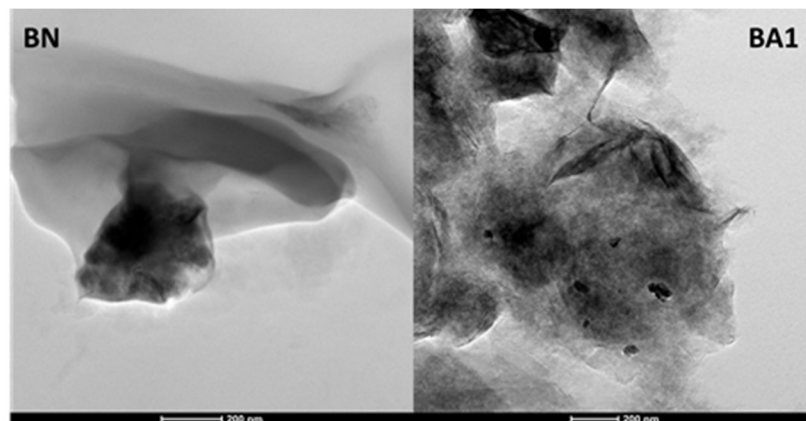


Figure 4. HRTEM micrographs of BN and BA1. Scale bars indicate 200 nm.

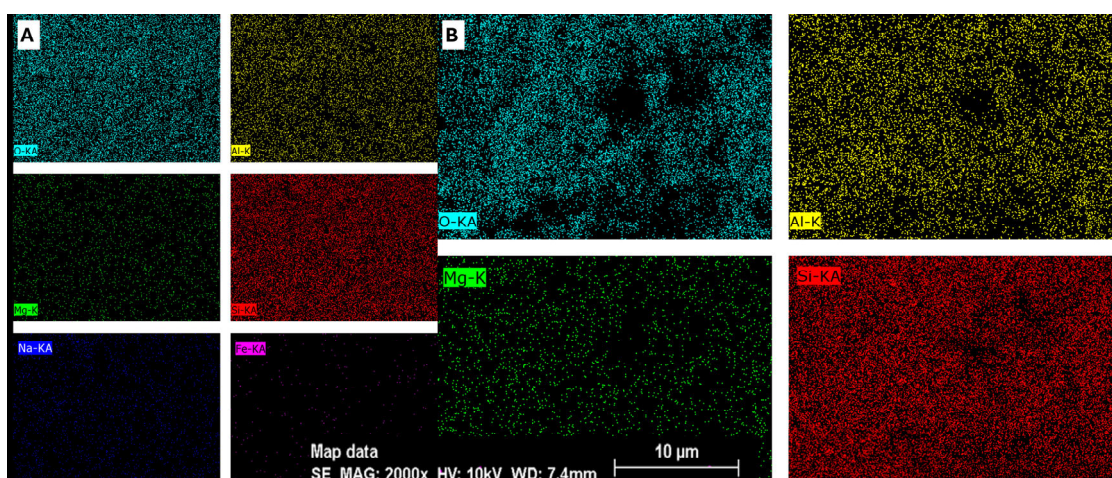


Figure 5. EDX elemental mapping of BN (A) and BA1 (B). Scale bars indicate 10 μm .

3.4. Textural Analysis by N_2 Adsorption–Desorption Isotherms

The N_2 adsorption–desorption isotherms at 77 K for the BN, BNF, BA1, and BA1F samples are shown in Figure 6. According to the IUPAC classification, these isotherms are type IV with H2 hysteresis loops ($P/P_0 > 0.9$), characteristic of mesoporous materials. The presence of hysteresis in the intermediate regions of relative pressure (P/P_0) indicates pores with a heterogeneous distribution. The BA1 sample exhibited the highest surface area ($165 \text{ m}^2 \cdot \text{g}^{-1}$) and pore volume ($0.15 \text{ cm}^3 \cdot \text{g}^{-1}$), suggesting a highly porous structure favorable for adsorption processes, confirming that the applied treatment significantly influenced its morphology. The average pore diameter varied among the samples, with values ranging from 32.67 to 43.78 Å. The BNF sample exhibited the largest pores (43.78 Å), while BA1F showed the smallest (32.67 Å) [15,16]. These results demonstrate that the BA1 sample has better characteristics for applications involving adsorption due to its higher surface area and pore volume, as observed in Table 2 [16,17].

Table 2. N_2 adsorption data of the samples.

Samples	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_p^a ($\text{cm}^3 \cdot \text{g}^{-1}$)	Pore Diameter (Å)
BN	63	0.06	37.43
BNF	17.8	0.02	43.78
BA1	165	0.15	35.29
BA1F	121	0.09	32.67

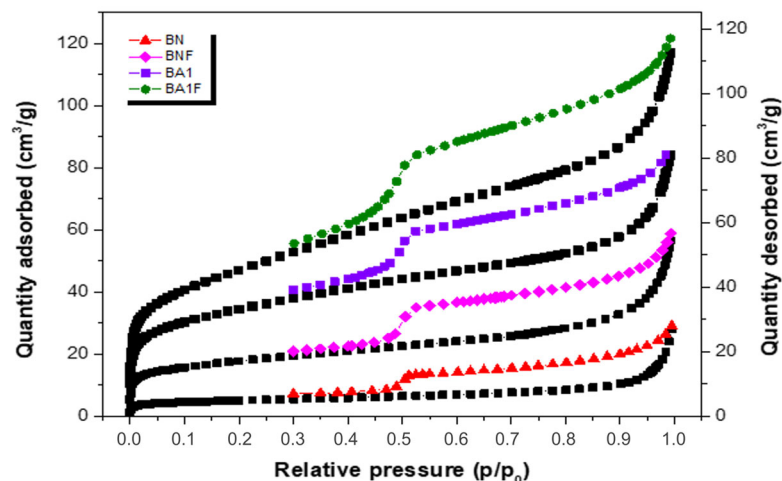


Figure 6. N_2 adsorption isotherms of BN, BNF, BA1, and BA1F samples.

3.5. X-Ray Photoelectron Spectroscopy

The deconvolution of the XPS spectra (Figure 7) is directly related to the materials' ability to adsorb tetracycline. The adsorption process is strongly influenced by the interactions between the functional groups present in the adsorbents and the antibiotic molecules. In the C 1s spectra, the BA1F, BA1, and BNF samples exhibit characteristic signals of C–C/C–H (Csp^3) bonds and oxygenated groups such as C–OH and O–C=O. These functional groups are crucial for tetracycline adsorption, as they interact with the antibiotic's amino and oxygenated functionalities through hydrophobic interactions, hydrogen bonds, and van der Waals forces, thereby enhancing the adsorption capacity of the materials [18].

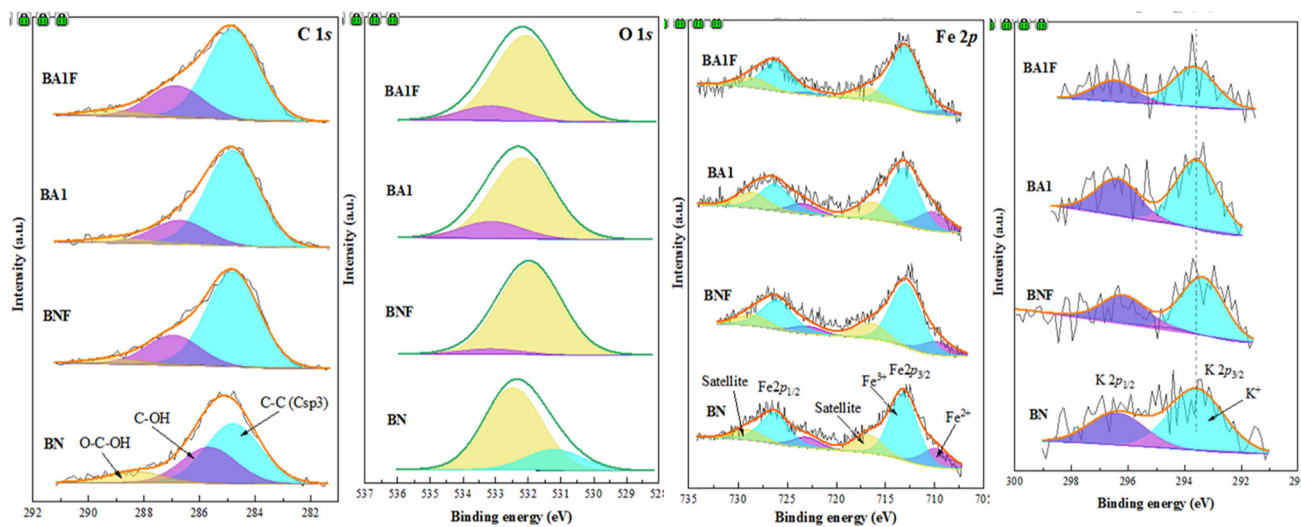


Figure 7. Deconvoluted high resolution C 1s, O 1s, Fe 2p and K 2p core level spectra for samples BN, BNF, BA1 and BA1F.

The O 1s spectra indicate the presence of oxygen bonded to carbonyl (C=O) and hydroxyl (C–O) groups in all samples, which are essential for adsorption as they enable the formation of hydrogen bonds with tetracycline. The BN material exhibits oxygen peaks with higher intensity, suggesting stronger interactions with tetracycline and, consequently, more efficient adsorption [19]. Additionally, the presence of iron oxides, particularly Fe^{2+} and Fe^{3+} , in the BA1F, BA1, and BNF samples contributes to an increased affinity of these materials for tetracycline. These species interact with the antibiotic's functional groups,

providing additional active sites for adsorption [20,21]. Finally, the K 2p spectra reveal the presence of potassium, particularly in the BN sample.

3.6. CO₂ Adsorption–Desorption Isotherms

The analyzed materials exhibit varying CO₂ adsorption capacities, with the BA1 material showing a higher adsorption capacity compared to BN, which displays the lowest adsorption capacity. The CO₂ adsorption isotherms of the materials, indicated by black symbols, are associated with the desorption isotherms presented in different colors in the legend. This suggests a lower affinity between CO₂ and the surface of BN (Figure 8). This variation may be related to structural and textural differences among the materials, such as the specific surface area, pore size, and presence of active functional groups on the surface, which is consistent with previous results. The hysteresis observed between the adsorption and desorption cycles indicates the presence of mesoporous structures in the materials, with CO₂ retention occurring due to capillary effects within the pores. The deviation between the adsorption and desorption curves is more pronounced in materials with higher adsorption capacity, suggesting that CO₂ interaction with the surface may involve diffusion processes and entrapment in narrow pores [22–24].

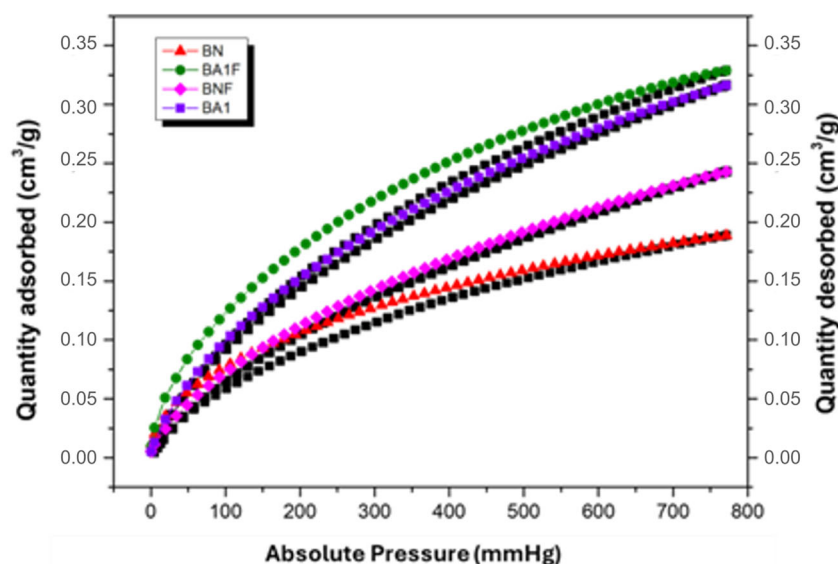


Figure 8. CO₂ adsorption isotherms of BN, BA1F, BNF, and BA1 samples.

3.7. Thermogravimetric Analysis (TGA/DTG)

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the BN, BNF, BA1, and BA1F samples (Figure 9) reveal two main mass loss events. The first event occurs around 100 °C and is associated with the elimination of adsorbed and interlayer water, indicating a significant presence of structural water in the samples. During this phase, the thermogravimetric mass loss is approximately 8.52%, suggesting a high moisture content and a strong interaction between water and the material's structure—an intrinsic characteristic of this material. The second significant mass loss event occurs around 740 °C, associated with the structural degradation and dehydroxylation of the material. At this stage, the hydroxyl groups in the crystalline structure are removed as water molecules, resulting in an endothermic peak and mass loss of around 447.5 °C. The mass loss at this stage is approximately 0.53%. The dehydroxylation temperature of the samples serves as an indicative parameter for the thermal resistance and structural stability of the analyzed materials. No clear evidence of total amorphization is observed, suggest-

ing that the material retains part of its structural properties even after high-temperature thermal treatment [25].

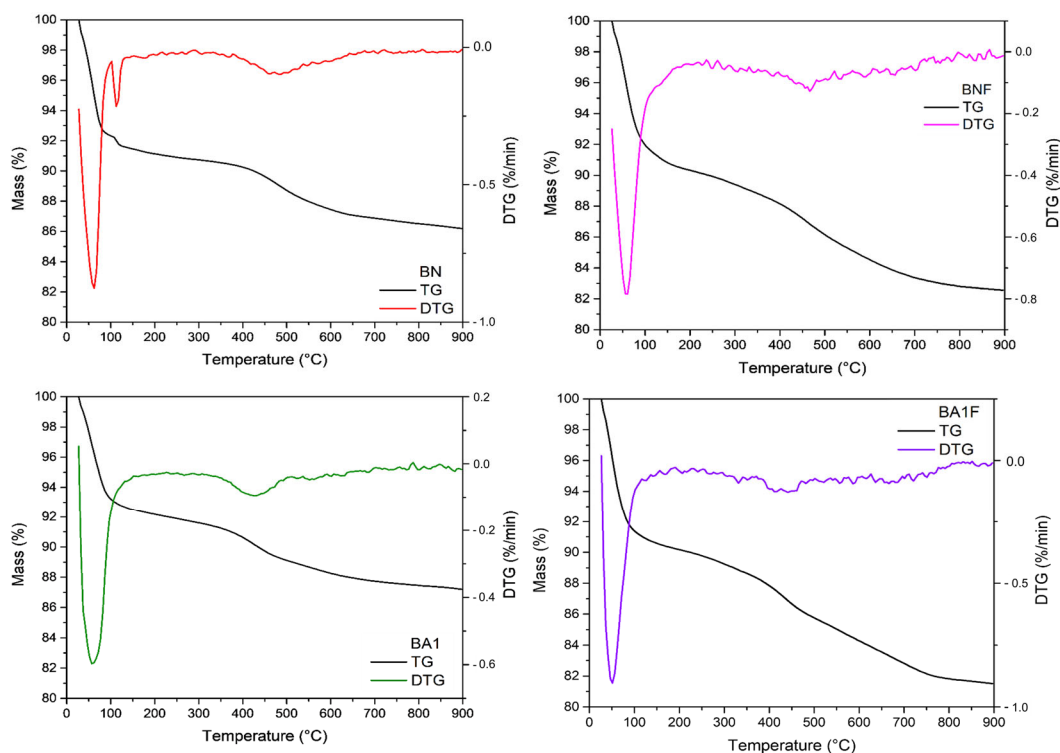


Figure 9. Thermogravimetric analysis (TG/DTG) of BN, BNF, BA1, and BA1F samples.

3.8. TC Adsorption Kinetics

The evaluation of adsorption kinetics reveals (Figure 10 and Table 3) that BA1 exhibits the highest experimental adsorption capacity ($q_e = 41.35 \text{ mg}\cdot\text{g}^{-1}$) at 30 min, with a drug concentration (C_e) of $500 \text{ mg}\cdot\text{L}^{-1}$. Adsorption studies with BA1 ($q_e = 40.98 \text{ mg}\cdot\text{g}^{-1}$) show a slight increase in the amount of tetracycline adsorbed compared to BN ($q_e = 40.60 \text{ mg}\cdot\text{g}^{-1}$), highlighting the effectiveness of acid treatment in enhancing tetracycline adsorption. Figure S1 in the Supplementary Material depicts the maximum adsorptive capacity of BN and BA1 adsorbents as a function of time for the adsorption TC, and the experimental data for the adsorption kinetics are summarized in Tables S1 and S2.

Table 3. Parameters for the fitting to pseudo-first-order, pseudo-second-order, and Elovich models.

Kinetic Parameters	BN	BA1
$q_{e,\text{exp}} (\text{mg}\cdot\text{g}^{-1})$	3.84	4.08
Pseudo-first order		
$k_1 (\text{min}^{-1})$	−0.0008	−0.0026
$q_{e,\text{cal}} (\text{mg}\cdot\text{g}^{-1})$	0.271	0.483
R^2	0.9799	0.848
Pseudo-second order		
$k_2 (\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1})$	0.0071	0.1232
$q_{e,\text{cal}} (\text{mg}\cdot\text{g}^{-1})$	3.87	4.04
R^2	0.9998	0.9998
Elovich		
$\alpha (\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1})$	7.30×10^{-5}	1.30×10^{-2}
$\beta (\text{g}\cdot\text{mg}^{-1})$	0.309	0.906
R^2	0.9681	0.9679

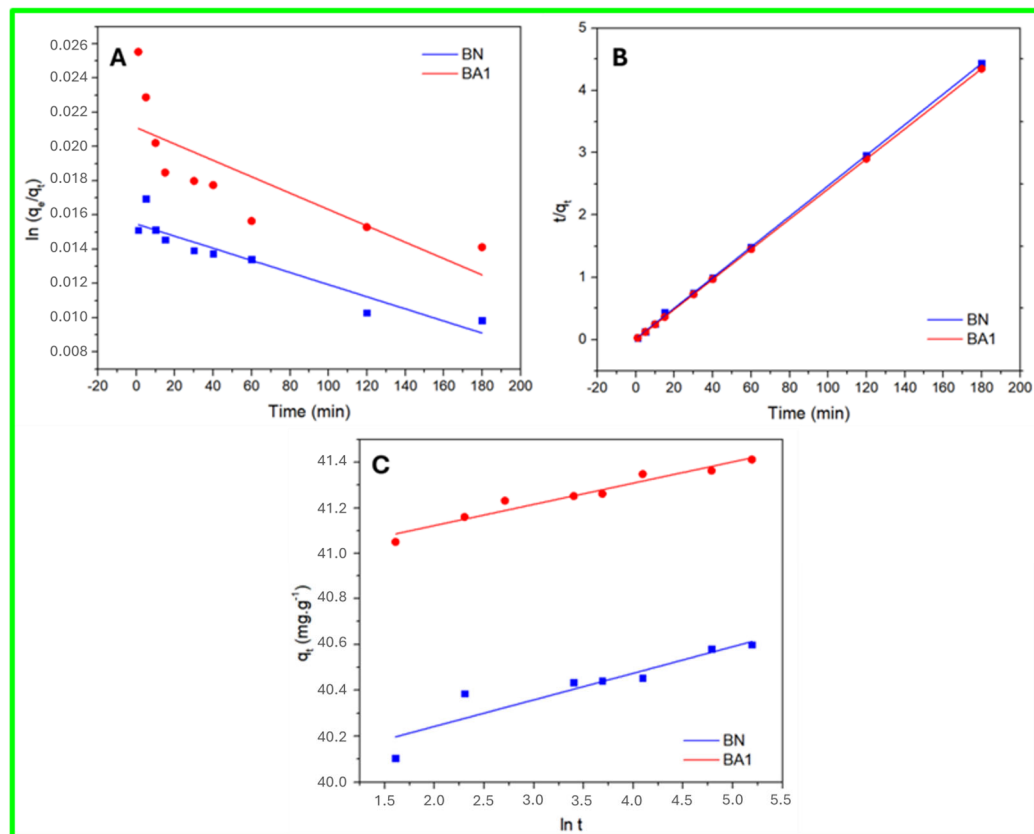


Figure 10. Adsorption kinetics data for BN and BA1 samples fitted to pseudo-second-order (A), pseudo-first-order (B), and Elovich (C) models.

Among the three models studied, the pseudo-second-order model exhibited the best fit to the data, with a coefficient of determination close to 1 ($R^2 = 0.999$). This model showed a minimal difference between the experimental ($41.35 \text{ mg} \cdot \text{g}^{-1}$) and calculated ($40.98 \text{ mg} \cdot \text{g}^{-1}$) q_e values, suggesting that chemisorption is the rate-determining step in the tetracycline adsorption process, involving electron exchange or sharing between the adsorbent and adsorbate [26]. The kinetic parameters derived from the pseudo-second-order model are critical for understanding the adsorption mechanism. The parameter k_2 represents the adsorption rate or the speed at which the adsorbate interacts with the adsorbent. As shown in Table 3, BA1 exhibits a higher adsorption rate than BN, indicating faster and more efficient adsorption compared to the natural clay [5].

The Elovich equation was applied to describe the adsorption kinetics; however, the model showed a poor fit for BA1 ($R^2 < 0.9412$), indicating that it did not adequately capture the variability of the experimental data. As shown in Figure 10, the adsorption capacity (q_t) increases with $\ln t$, but the data for BA1 exhibit a higher initial adsorption capacity compared to BN. The Elovich model is often used to describe chemisorption on heterogeneous surfaces, where the parameter α represents the initial adsorption rate, and β reflects the extent of surface activation over time. The relatively low correlation observed for this model suggests that the adsorbent surfaces do not exhibit extreme heterogeneity, reinforcing the predominance of controlled chemisorption mechanisms. Additionally, the lower slope observed for BN suggests a slower adsorption process compared to BA1, which exhibited a steeper increase in q_t , indicating a more efficient adsorption performance in the evaluated time range [27].

The pseudo-first-order model showed MSE values of 0.00413 for BN ($R^2 = 0.7701$) and 0.01391 for BA1 ($R^2 = 0.56192$). The pseudo-second-order model, which best describes the adsorption process, presented MSE values of 0.001538 for both BN and BA1 ($R^2 = 0.9998$).

The Elovich model showed MSE values of 0.000054 for BN ($R^2 = 0.9679$) and 0.000057 for BA1 ($R^2 = 0.9681$). These results reinforce the superiority of the pseudo-second-order model, confirming that the adsorption process is primarily controlled by chemisorption [28,29].

3.9. TC Adsorption Isotherms

To describe the relationship between the adsorbent and adsorbate at equilibrium for varying initial concentrations, Langmuir, Freundlich, Sips, and Temkin isotherm models were applied, as illustrated in Figure 11. The parameters derived from these models provide insight into the adsorption mechanism and the specific surface properties of the materials.

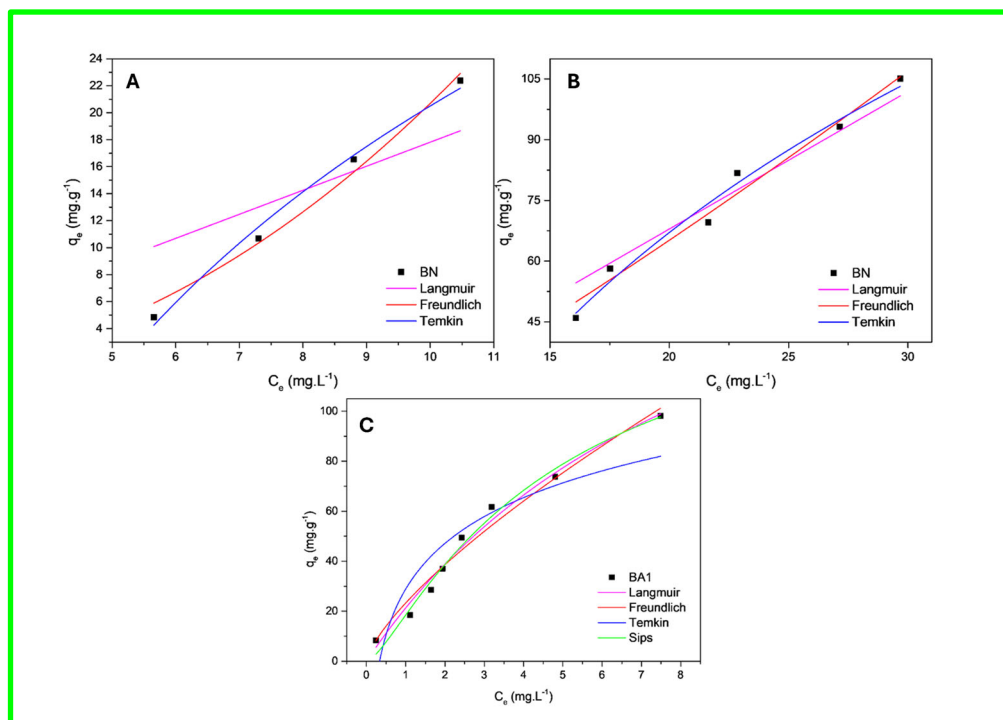


Figure 11. Equilibrium isotherms for BN at low concentrations (A) and high concentrations (B) and BA1 (C).

The Langmuir model assumes monolayer adsorption on a surface with a finite number of identical sites, where the adsorption energy remains constant. The parameter q_m represents the maximum adsorption capacity, and for BA1, a q_m of $110 \text{ mg} \cdot \text{g}^{-1}$ was reached in 30 min at a C_e of $43.46 \text{ mg} \cdot \text{L}^{-1}$. This suggests that BA1 possesses a high density of active sites, enhancing its adsorption potential. The Langmuir constant (K_L) reflects the affinity between the adsorbate and adsorbent, with a higher K_L value indicating stronger interactions on the material's surface. For BA1, a K_L value of 0.23 was obtained, signifying stronger chemical interactions with tetracycline (TC) compared to BN. The enhanced interaction is due to the acid treatment that leaches surface impurities, exposing more active groups for interaction, thus favoring chemisorption as the dominant mechanism [30,31].

For BN, the equilibrium data were analyzed at both low and high concentrations (Figure 11A,B). At low concentrations (Figure 11A), the Langmuir and Freundlich models provided good fits to the experimental data, suggesting that both monolayer adsorption and multilayer adsorption phenomena occur. However, at higher concentrations (Figure 11B), the Langmuir model exhibited a superior fit, indicating that monolayer adsorption becomes the predominant mechanism as the available active sites become more occupied. The discrepancy observed for the Temkin model at lower concentrations suggests that the assumption of a uniform decrease in adsorption energy may not hold under these conditions.

The Freundlich model, which describes adsorption on heterogeneous surfaces and the formation of multilayers, was also considered. The parameter K_F in this context represents the adsorption capacity, while the exponent n provides insight into adsorption intensity. Experimental data show that BA1 exhibited a Freundlich exponent ($1 < n < 10$), confirming a favorable adsorption process. Additionally, the relatively high K_F value obtained for BA1 further supports a strong affinity for TC, reinforcing the presence of heterogeneous adsorption sites and the suitability of the adsorbent for tetracycline uptake [32,33]. In Figure 11A,B, the Freundlich model suggests that BN also exhibits surface heterogeneity, though its fit varies depending on concentration. The better fit at lower concentrations supports the presence of multiple types of adsorption sites, while the deviation at higher concentrations suggests a shift toward monolayer saturation.

The Sips (Simplified Modified Langmuir–Freundlich) model, which combines elements of both the Langmuir and Freundlich models, accounts for surface heterogeneity while still considering the possibility of monolayer adsorption at higher adsorbate concentrations. The excellent fit of the Sips model to the data ($R^2 = 0.9767$ for BA1 and for BN, the model did not converge) indicates that both materials exhibit moderate surface heterogeneity and substantial interaction with the adsorbate. The equilibrium constant K_S from the Sips model quantifies the affinity between the adsorbate and adsorbent. A higher K_S value for BA1 suggests a more optimized balance between surface heterogeneity and adsorption capacity, implying that this material possesses better overall adsorption characteristics than BN. These findings are consistent with previous studies in the literature, reinforcing the significance of surface modification through acid treatment to enhance adsorption capacity [33,34].

The Temkin model, which assumes that adsorption energy decreases as sites become occupied, further supports these observations. In this model, the constant B reflects the distribution of adsorption energy, and the parameter A_T represents the binding energy of the adsorbent. The Temkin model suggests that initial adsorption interactions are strong, gradually weakening as more sites are occupied. For BA1 (Figure 11C), these parameters indicate that the adsorption process is energetically favorable in the early stages, reinforcing the role of both physisorption and chemisorption in the adsorption of tetracycline. However, for BN (Figure 11A,B), the Temkin model did not fit as well as the other models, likely due to the assumption that adsorption energy decreases uniformly across all adsorption sites, which may not fully capture the heterogeneity of BN.

Taken together, the isotherm analysis confirms that BA1 exhibits a heterogeneous but highly efficient adsorption surface, making it an ideal candidate for applications involving tetracycline removal, with significant contributions from both physical and chemical adsorption mechanisms. Meanwhile, BN demonstrates concentration-dependent adsorption behavior, with heterogeneity playing a more prominent role at lower concentrations and monolayer adsorption becoming more dominant at higher concentrations.

A comparison of various studies on tetracycline adsorption reported in the literature, emphasizing factors such as isotherm and kinetic models applied, type of adsorbent, removal efficiency, and time required to reach adsorption equilibrium, is summarized in Table 4.

Table 4. Comparative analysis of tetracycline hydrochloride adsorption.

Clay Mineral	Isotherm	Kinetics	Time (min)	Removal (%)	Author
BN	Freundlich	Pseudo-second order	30	97	This study
BA1	Freundlich	Pseudo-second order	30	99	This Study
Nano montmorillonite	Langmuir	Pseudo-first order	60	90	[4]
20% In ₂ O ₃ /Halloysite	Langmuir	Pseudo-second order	60	98	[35]

Table 4. Cont.

Clay Mineral	Isotherm	Kinetics	Time (min)	Removal (%)	Author
25% In ₂ O ₃ /Halloysite	Freundlich	Pseudo-second order	1440	88.3	[36]
Carbon–Cu composite	Langmuir	Pseudo-second order	120	75	[37]
Bentonite	Langmuir	Pseudo-second order	1440	-	[9]
Orange biocarbon	Langmuir	Pseudo-second order	16	57.69	[38]
Magnetic bentonite/CMC	Langmuir	Pseudo-second order	120	96	[39]

3.10. Adsorbent Recycling Assessment

The adsorbents BN and BA1 exhibit significant performance in the removal of TC across consecutive adsorption cycles (Figure 12), with a minor decline in adsorption efficiency (10–14%) after seven reuse cycles. This demonstrates that the methodology developed in this study is both effective and reliable, preserving the functionality of the adsorbents at a satisfactory level throughout the recycling process in wastewater treatment, with particular emphasis on the BA1 material. Moreover, large-scale implementation needs careful planning to ensure that the efficiency observed in laboratory conditions is maintained under varying flow rates and pollutant loads. Therefore, the adaptation of these materials for real-world wastewater treatment applications must consider not only their removal capacity but also their chemical stability, as well as the costs associated with regeneration and the safe disposal of generated waste, as highlighted in the literature for real cases of wastewater treatment [40–42].

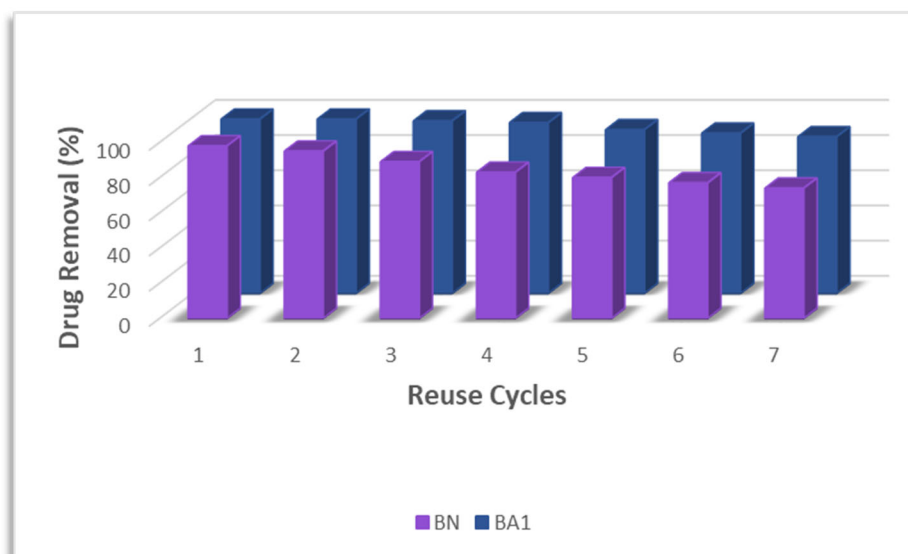


Figure 12. Reuse of BN and BA1 adsorbents after drug adsorption.

4. Conclusions

This study underscores the potential of bentonite-based materials as effective and sustainable adsorbents for removing contaminants from pharmaceutical effluents, aligning with the United Nations' 2030 Agenda, specifically SDG 12 on Responsible Consumption and Production. Among the tested adsorbents, acid-treated bentonite exhibited enhanced adsorption capacity compared to its natural form. Notably, BA1 demonstrated similar adsorption performance to BA2.5, an adsorbent subjected to acid treatment with 2.5 mol·L^{−1} HCl, while requiring a lower acid concentration. This reduction minimizes reagent consumption and waste generation while maintaining high removal efficiency.

Advanced characterization techniques, including XPS, XRF, EDS, SEM, and TEM, revealed a silicon- and aluminum-rich composition. Acid treatment significantly improved

surface properties, increasing surface area and functional group availability. The reuse analysis demonstrates that BA1 maintained high removal efficiency over multiple cycles, indicating its robustness and suitability for continuous wastewater treatment applications. Kinetic studies confirmed that optimal adsorption conditions for BA1 were achieved within 30 min using 0.30 g of adsorbent, following a pseudo-second-order kinetic model and Freundlich isotherm, suggesting a mixed adsorption mechanism involving chemisorption and physisorption.

These modifications not only enhanced the adsorption of pharmaceutical contaminants, such as tetracycline hydrochloride, but also demonstrated the versatility of bentonite in addressing diverse industrial and environmental challenges. Overall, this work highlights bentonite as a readily available, eco-friendly material with significant potential for sustainable applications in the pharmaceutical industry, particularly in the development of reusable, high-efficiency adsorbents.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app15063372/s1>, Figure S1. Maximum adsorptive capacity of BN and BA1 adsorbents as a function of time for the adsorption TC. Table S1: Kinetic data related to the BN adsorbent; Table S2: Kinetic data related to the BA1 adsorbent

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