

Removal of Tetracycline from Aqueous Solutions Using Avocado Peel-Based Biochar

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Abstract:- Tetracycline (TC), a widely used antibiotic, is increasingly found in aquatic environments, posing significant risks to ecosystems and human health. Therefore, this study aimed to evaluate TC removal using alkaline-modified biochar (BioCH-M) derived from avocado peels. The methodology involved pyrolysis of avocado peels, alkaline hydrothermal treatment, comprehensive characterization using techniques such as Scanning Electron Microscopy (SEM) and Fourier-Transform Infrared Spectroscopy (FTIR), batch adsorption experiments for kinetic and equilibrium studies, and data fitting to kinetic and isotherm empirical models. The results showed that BioCH-M exhibited a high adsorption capacity (45.05 mg/g at 25°C) for tetracycline, with optimal adsorption occurring at slightly acidic to neutral pH. The adsorption process was rapid and reached equilibrium quickly (300 min). The Langmuir isotherm model suggested that TC molecules occupy specific sites on the biochar surface, and the temperature effect indicates that the adsorption process is endothermic. This study demonstrates that BioCH-M is an effective and sustainable adsorbent for removing tetracycline from aqueous solutions, highlighting the potential of waste biomass to produce biochar as a viable solution to treat pharmaceutical pollution in water bodies.

Keywords:- Tetracycline; Biochar; Adsorption; Pharmaceutical Contaminants; Avocado Peel.

I. INTRODUCTION

The increasing prevalence of pharmaceutical contaminants in aquatic environments has become a critical concern for environmental scientists and public health officials. They pose a significant environmental and health problem due to their potential adverse effects on ecosystems and human health. These compounds, including antibiotics like sulfamethoxazole and tetracycline, are commonly found in surface water, groundwater, and wastewater effluents [1]. They are often detected at low concentrations but are widespread due to extensive human and veterinary medicine use [2].

Pharmaceuticals in water can disrupt aquatic ecosystems by affecting microbial populations, leading to the disappearance of key microbial groups. The persistence of these compounds in the environment can lead to bioaccumulation and biomagnification, posing risks to aquatic organisms and potentially entering the human food chain [1], [3]. Human health risks include chronic exposure and the development of antibiotic-resistant bacteria. Studies have indicated mutagenic and genotoxic effects, which could have long-term health implications for humans.

Among these contaminants, tetracycline (TC), a widely used antibiotic, poses significant risks due to its potential to contribute to antibiotic resistance in bacteria, leading to treatment failures in both human and veterinary medicine. Tetracycline is frequently detected in wastewater and surface water due to its extensive use in agricultural activities and human medicine. It can inhibit the growth of algae and plankton, which are essential components of aquatic ecosystems. High concentrations of tetracycline can cause significant growth inhibition and structural changes in algal cells, affecting the entire food chain. It can also cause embryotoxicity in fish, such as zebrafish, by inducing oxidative stress and apoptosis, leading to developmental issues [4]. Tetracycline can disrupt endocrine functions in aquatic species, such as fish, by causing the production of vitellogenin, a protein associated with reproductive processes. This can lead to antibiotic resistance, spreading rapidly among microbial populations and eventually reaching human pathogens [5]. The spread of antibiotic-resistant bacteria in water systems directly threatens human health, as they can enter drinking water supplies and agricultural systems, increasing the risks of difficult-to-treat infections [6]. The World Health Organization (WHO) has recognized antibiotic resistance as one of the most pressing global health challenges, emphasizing the need for effective strategies to manage antibiotic contamination in the environment. Its persistence in the environment raises alarms about the efficacy of conventional wastewater treatment processes, which often fail to remove such pharmaceutical compounds adequately. Consequently, there is an urgent need for innovative and effective methods to remove tetracycline from contaminated water sources.

There are different methods to remove emerging or pharmaceutical contaminants from natural and wastewater; among them, adsorption is one of the most effective and efficient methods, mainly when the concentrations of these contaminants are low. This process has gained attention as a promising technique for removing tetracycline from aqueous solutions due to its simplicity, cost-effectiveness, and high efficiency. This method involves the adherence of tetracycline molecules onto the surface of adsorbent materials, which can be derived from natural or synthetic sources. The effectiveness of adsorption depends on various factors, including the nature of the adsorbent, solution pH, contact time, initial concentration of tetracycline, and temperature. Its ability to form stable complexes with metal ions further complicates its removal from water. Advanced treatment methods like ozonation and photolysis have been explored for tetracycline removal, but they can be costly and may produce toxic byproducts. These challenges highlight the need for more effective and sustainable methods to remove tetracycline from the environment [4], [5], [6]. Several studies have explored different adsorbent materials ranging from activated carbon to biochar and metal-organic frameworks (MOFs), each exhibiting unique properties that influence their adsorption capacities [6], [7]. Thus, removing tetracycline from contaminated water through adsorption presents a viable solution to mitigate environmental pollution and public health risks associated with antibiotic residues. Ongoing research into various adsorbent materials continues to provide insights into optimizing adsorption processes for enhanced efficiency. As awareness grows regarding the implications of pharmaceutical pollutants in aquatic systems, further exploration into sustainable and effective removal techniques will be essential for safeguarding water quality and public health. In summary, addressing tetracycline contamination requires a multifaceted approach combining advanced materials science with environmental engineering principles. Continued innovation in adsorptive technologies will play a pivotal role in developing effective strategies for managing pharmaceutical residues in our water systems.

Biochar is a promising material for removing contaminants like tetracycline from aqueous environments due to its cost-effectiveness and efficiency. Its surface functionality and porosity enhance its ability to adsorb pollutants like tetracycline. Adsorption mechanisms involve electrostatic interactions, hydrogen bonding, and π - π electron donor-acceptor interactions [2]. The optimal adsorption occurs at mildly acidic to neutral pH levels where tetracycline exists in zwitterionic form. Composite materials like montmorillonite can enhance biochar's adsorption capacity for tetracycline. Modified biochar, treated with acids or loaded with metals, can improve adsorption efficiency [8]. Biochar is derived from waste biomass, making it a sustainable and low-cost option for water treatment applications. The production and use of biochar support waste management and resource recovery, contributing to environmental sustainability. Challenges in current applications include limitations in its adsorption capacity due to competing ions in water and the specific characteristics of the biochar used. Future research should focus on optimizing biochar properties and exploring

integrated treatment systems to enhance their application in environmental remediation.

Therefore, the present study aimed to evaluate the removal capacity of tetracycline, an emerging contaminant, using a modified hydrothermal biochar (BioCH-M) produced from avocado peels in a batch reactor. The adsorbent material was characterized, the process conditions were optimized to maximize removal efficiency, and the interaction mechanisms between biochar and tetracycline were analyzed. In addition, the kinetic, equilibrium, and thermodynamic parameters associated with the adsorption process were determined, providing a sustainable approach for mitigating pharmaceutical contaminants in water.

II. MATERIALS AND METHODS

A. Biochar Preparation

The pyrolysis process is a thermochemical treatment without oxygen at high temperatures. Biochar is obtained according to the process conditions and the raw material. In this case, avocado peels, previously treated to remove impurities, were used to get the biochar. This process was carried out in a Thermo Scientific tubular oven, with a constant flow of nitrogen gas (2 mL/min) until reaching a temperature of 500 °C with a heat ramp of 10 °C per minute, maintaining the temperature for 65 minutes, and then it was allowed to cool to room temperature without the circulation of nitrogen gas. The hydrothermal chemical post-treatment of the biochar was carried out with a 2M NaOH solution, stirring it in a thermo-bath (Thermo Electron Corporation brand) for 2 hours at a constant temperature of 60 °C. The activated biochar was filtered and rinsed several times with deionized water to remove any excess reagent. The biochar was allowed to dry in an oven at 40°C, identified as BioCH-M, and used without further treatment in tetracycline (TC) adsorption tests.

B. Biochar Characterization

Fourier Transform Infrared Spectroscopy (FTIR) was used to determine the absorption bands of functional groups of organic and inorganic compounds within the BioCH-M structure. FTIR analyses were performed on BioCH-M samples before and after TC removal. The apparatus employed was a Bruker Mid-FTIR, equipped with a fiber optic probe, which directly examines the adsorbent surface. The spectral range extended from 4000 to 400 cm^{-1} , with a resolution of 4 cm^{-1} . The BioCH-M was pulverized and combined with KBr to create pellets for each biosorbent sample, facilitating the identification of the significant bands in the spectrogram.

Furthermore, Scanning Electron Microscopy (SEM) was also used to examine and characterize the surface properties of BioCH-M, focusing on its texture, pore size, morphology, and semi-quantitative elemental composition through energy dispersive spectroscopy (EDS) analysis. The samples were coated with copper and examined using a scanning electron microscope (JEOL JMS-6400, JEOL Ltd., Peabody, MA, USA) integrated with an EDS microanalysis detector (Bruker XFLASH 4010, Peabody, MA, USA).

C. Adsorption Kinetics

Batch contact studies were performed using TC solutions with different contact durations to determine their adsorption kinetics. In these experiments, 13 mL aliquots of a 20 mg/L TC solution were used and individually mixed with 50 mg of BioCH-M in polyethylene flasks. The samples were then placed in a thermal bath with shaking for different durations (from 30 to 480 min), rotating at 100 rpm and a temperature of 25 °C. Upon reaching the designated contact time, the supernatants were isolated by filtration. TC concentrations were quantified by UV-Vis spectroscopy (S2100UV, UNICO Systems Inc.), which facilitated the determination of the equilibrium time. All adsorption studies were performed three times to ensure repeatability. A control test without BioCH-M was conducted to assess analyte (TC) losses by mechanisms not related to adsorption. The kinetic data of Tetracycline on BioCH-M were analyzed using empirical mathematical models to characterize the adsorption kinetics of TC on the modified biochar. A non-linear regression analysis was conducted with Statistica 7.0 software to select the best-fitting model.

D. Influence of pH on Adsorption

Adsorption tests were performed with TC solutions at different pH levels individually to determine the pH value that resulted in maximum adsorbate removal and to assess the impact of this parameter on the biosorbent material. The process involved weighing BioCH-M (50 mg), placing them in polyethylene flasks, and adding 10 mL of a 20 mg/L TC solution. The pH of each solution was modified using 0.1 M HCl or NaOH, as necessary, to achieve values between 2 and 9. The flasks were shaken in a thermal shaking bath at 100 rpm at 25 °C until adsorption equilibrium was reached. After the contact period, the solution was filtered. UV-Vis spectroscopy was used to determine the total TC concentrations in the supernatant.

E. Adsorption Isotherms

Batch contact experiments were carried out to determine the influence of TC concentrations on the adsorption process and then obtain the adsorption isotherms of Tetracycline. Thus, solutions were prepared at different concentrations of the emerging contaminant ranging from 10 to 120 mg/L of Tetracycline, taking 10 mL aliquots of each to put them in contact with 0.05 g Bio-CH-M. They were then stirred until equilibrium was reached at different temperatures (25, 35, and 40°C) without modifying the pH of the TC solutions. The data of the adsorption isotherms of Tetracycline on BioCH-M were interpreted by fitting the Langmuir and Freundlich mathematical models to describe the adsorption equilibrium of TC on the modified biochar, choosing the best model through a non-linear regression analysis, performed using the Statistica 7.0 software.

III. RESULTS AND DISCUSSION

A. SEM-EDS Analysis

Scanning electron microscopy (SEM) allowed us to establish the BioCH-M morphology and elemental chemical composition semi-quantitatively. Figures 1 and 2 show SEM images of the adsorbent, which reveal the structure observed at 100x (Figure 1a), in which the biochar grains are observed with an irregular and rough surface. This provides an overview of the surface structure. At 350x zoom (Figure 1b), the porosity of the particle can be observed, offering a closer look at the finer details of the material morphology.

In the micrograph in Figure 1a, the biochar exhibits a rough and heterogeneous surface texture, typical of biochars derived from lignocellulosic materials. The irregular morphology, with visible pores and voids, indicates partial degradation of organic matter during hydrothermal treatment or pyrolysis [9]. These porous structures are advantageous for adsorption applications as they provide a large surface area and numerous active sites for contaminant interaction. In the case of the SEM micrograph in Figure 1b, higher magnification reveals a more intricate porous network and finer structural details. The presence of micro- and mesopores is evident, which can be attributed to the thermal decomposition of cellulose, hemicellulose, and lignin in the avocado peel [10]. The bright regions observed could indicate the presence of mineral residues or modifications introduced during biochar preparation (e.g., functionalization or natural inorganic content in the precursor).

The surface morphology observed in these SEM micrographs aligns with studies on biochar derived from agricultural waste. Biochars typically exhibit various pore structures influenced by the precursor material and production conditions such as temperature, residence time, and atmosphere. Avocado peels, rich in organic polymers, are broken down during pyrolysis or hydrothermal treatment, leaving behind a carbonaceous structure with high porosity. The porous network and surface features observed in these micrographs make this biochar a promising material for contaminant adsorption, catalysis, or soil amendment applications. These features are particularly relevant for the adsorption of pharmaceutical contaminants such as tetracycline. The pores may even provide physical entrapment, while the surface chemistry facilitates interactions such as hydrogen bonding, π - π interactions, or electrostatic attraction with contaminant molecules. SEM micrographs reveal favorable structural features of cellulose-derived biochar, including a hierarchical pore network and significant heterogeneity, making it suitable for sustainable pollutant removal in environmental applications.

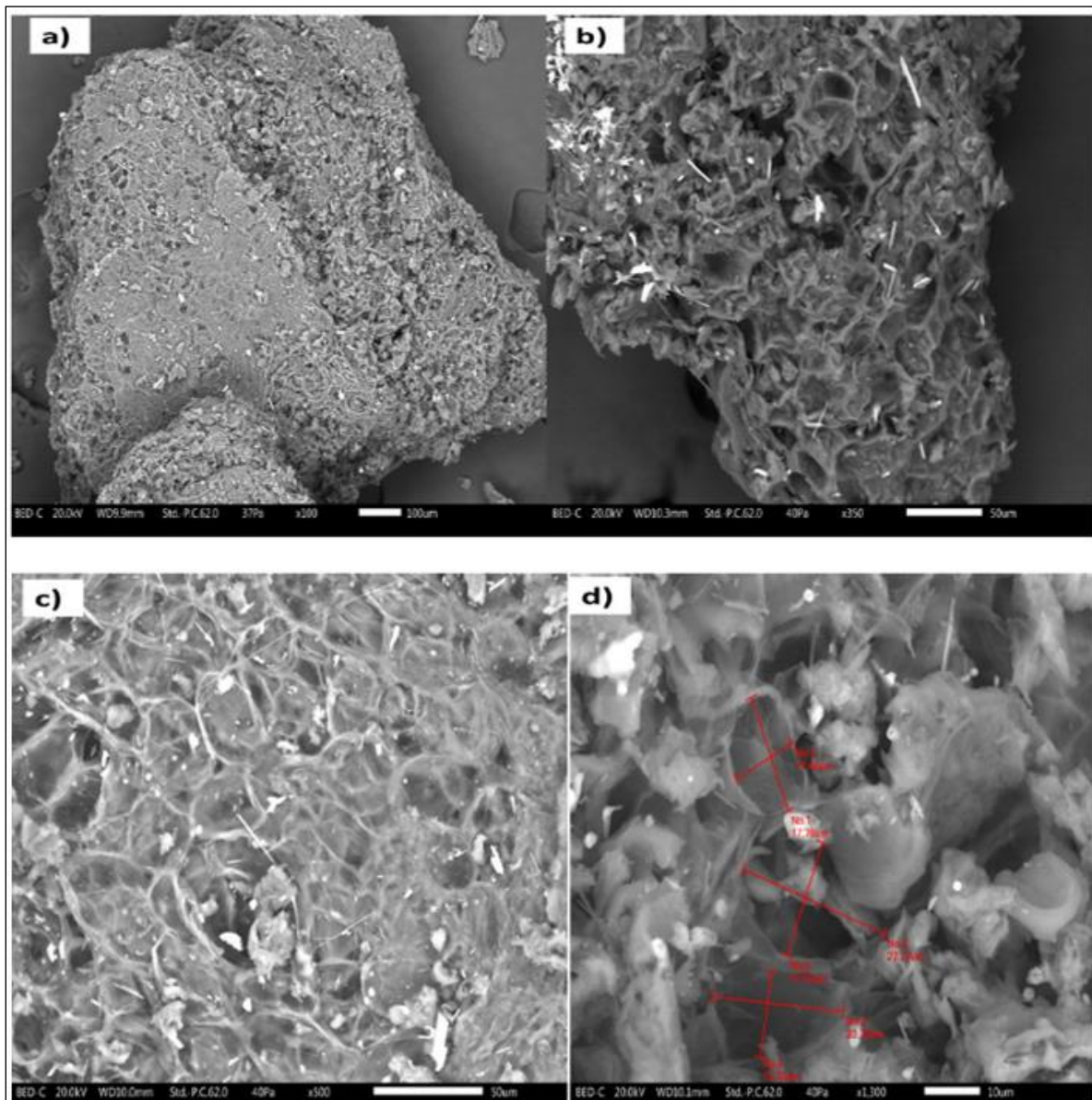


Fig. 1: SEM Micrographs of BioCH-M Grains Observed at (a) 100x, (b) 350x, (c) 500x, and (d) 1300x.

The same BioCH-M grains are observed at 500x (Figure 1c), where the different pore sizes and irregular zones are better detailed. Moreover, the pore sizes of the material are observed at 1300x (Figure 1d), ranging from approximately 17.7 μm to 27.2 μm ; this micrograph also provides a closer look at the biochar microstructure. It shows more detailed features, such as smaller pores and microcracks. The red lines and measurements delineate the dimensions of distinct features, emphasizing the variability in pore sizes and shapes. Moreover, a comprehensive microstructure examination elucidates the biochar's adsorption capabilities and mechanical properties [11]. Microcracks (Figure 1d) can influence the mechanical stability and durability of the biochar when used in various applications. A highly porous structure with interconnected networks of pores can also be observed in Figure 1c. The surface appears rough with various irregularities and cavities, which are typical biochar characteristics. The porous nature of biochar increases its surface area, making it effective in adsorbing contaminants.

On the other hand, to obtain chemical information about the adsorbent grains, an X-ray dispersion spectroscopy (EDS) microanalysis was performed where the main elements present in the BioCH-M sample were obtained; these are carbon (C), oxygen (O), calcium (Ca), magnesium (Mg), potassium (K), phosphorus (P) and sodium (Na). Figure 2 shows the graph showing the percentage values by weight of each element present. Carbon, with a percentage of 78.1%, is the most abundant element in said sample, followed by oxygen at 14.9%; the presence of potassium has a value of 5.2%; this concentration may be due to the residues of the chemical treatment that was carried out through the use of alkaline solutions. The presence of calcium, magnesium, phosphorus, sodium, sulfur, silica, aluminum, and chlorine can also be observed to a lesser extent. However, it is worth mentioning that the concentrations of these elements vary according to the conditions of the pyrolysis process and the composition of the raw material [12]. The presence of calcium (Ca) and magnesium (Mg) in biochars can enhance the

adsorption of antibiotics, mainly through improved structural and chemical properties. Calcium-rich biochar has shown significant potential in removing antibiotics like amoxicillin

from aqueous solutions, indicating that these elements play a crucial role in adsorption [13], [14].

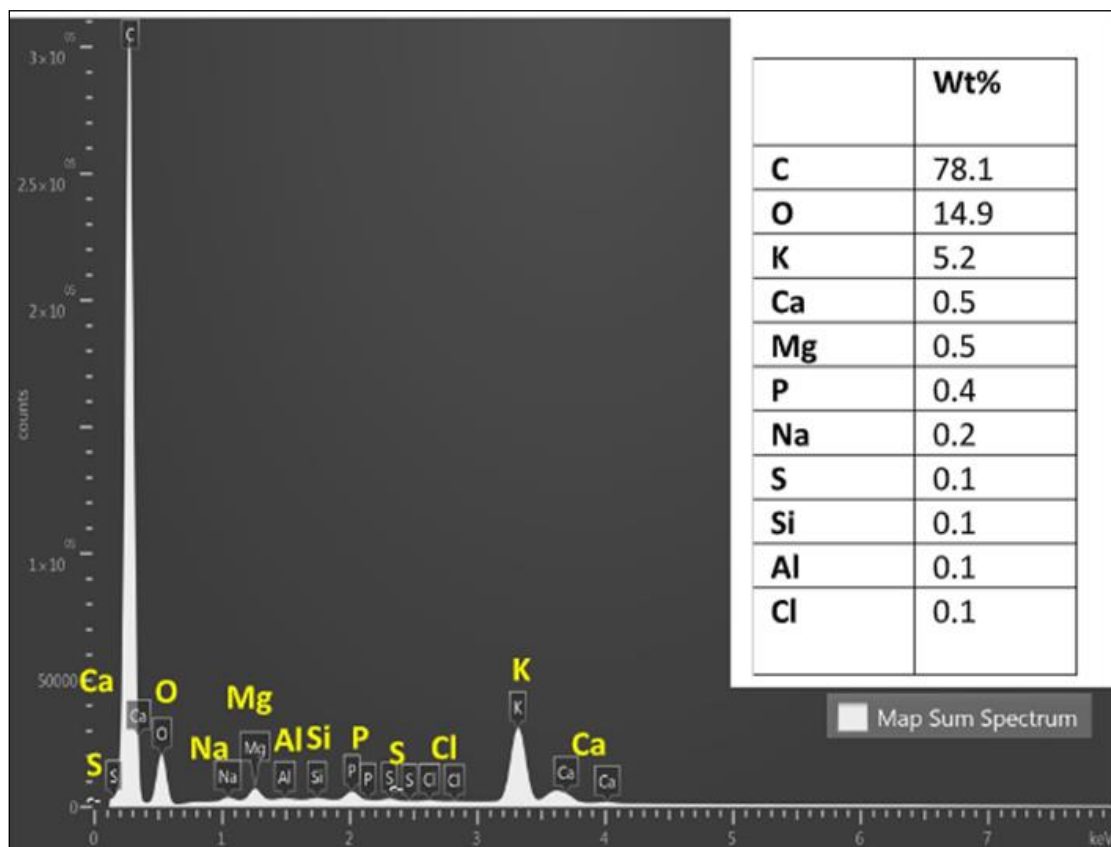


Fig. 2: EDS Analysis of BioCH-M.

B. FTIR Analysis

Figure 3 illustrates the FTIR spectra of BioCH-M before and after TC adsorption. A comparison of the FTIR spectra of the adsorbent shows significant changes in the functional groups after exposure to the contaminant. Notable differences in the functional bands are observed when comparing avocado peel biochar before (BioCH-M) and after tetracycline adsorption (BioCH-M-TC). Both spectra have a broad band near 3500-3000 cm^{-1} , associated with O-H bonds. In BioCH-M-TC, this band appears to decrease in intensity, which could suggest hydrogen interactions or the occupation of hydroxyl groups during TC adsorption. On the other hand, in the spectrum of BioCH-M-TC, an increase in the intensity and definition of the peak around 1700-1600 cm^{-1} , associated with the carbonyl group (C=O), is observed. This also suggests possible tetracycline interactions with carbonyl functional groups on the biochar surface. As for the alkene groups (C=C), in the region of 1500-1400 cm^{-1} , bands representing these bonds are seen, which appear more intense

or displaced in BioCH-M-TC, possibly due to π - π interactions between tetracycline and the aromatic structures of biochar [15]. The band around 1250-1000 cm^{-1} associated with ether groups (C-O-C) shows a slight change in intensity in BioCH-M-TC, suggesting interactions with tetracycline.

Furthermore, the peak in the low region, near 700-500 cm^{-1} (C-Cl), appears more prominent in BioCH-M-TC, which might be due to tetracycline residues. Also, the C-H bands in the 2900-2800 cm^{-1} region appear slightly less intense in BioCH-M-TC, indicating possible modifications in the hydrocarbon chains of biochar. Therefore, it can be established that tetracycline adsorption on BioCH-M induces significant changes in the regions associated with functional groups such as O-H, C=O, C=C, and C-O-C; this demonstrates the chemical and physical interactions between tetracycline and biochar, including hydrogen bonds, π - π interactions, and the formation of surface complexes.

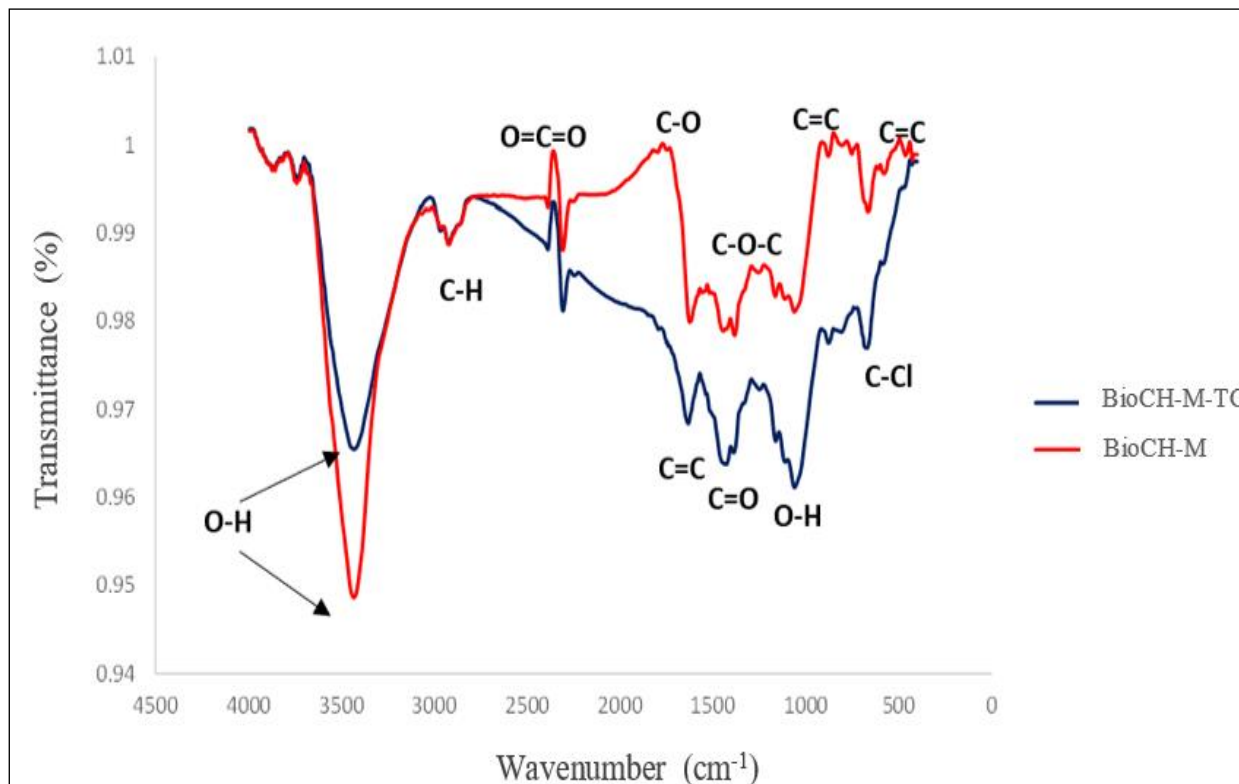


Fig. 3: FTIR Spectrograms of BioCH-M (red line) and BioCH-M-TC (blue line).

C. Adsorption Kinetics

Figure 4 shows the graph with the results of the removal kinetics of tetracycline with BioCH-M at a concentration of 20 mg/L for 480 minutes. The removal percentage was plotted against the sorption time at a temperature of 25°C. Figure 4 shows the graph with the results of the tetracycline removal kinetics with BioCH-M at a concentration of 20 mg/L for 480 minutes. The removal percentage was plotted against the adsorption time at a temperature of 25°C. A significant initial increase in the TC removal percentage is observed, reaching approximately 35% in the first 200 minutes. This suggests rapid initial adsorption, probably due to the high availability of active sites on the BioCH-M surface. Subsequently, the kinetics slowly approach equilibrium around 300 minutes, where the removal percentage stabilizes near 40%. The gradual decrease in the adsorption rate after 200 minutes

indicates a progressive saturation of the adsorbent's active sites. The observed behavior can be attributed to a two-stage adsorption mechanism: (i) a rapid initial phase, where surface diffusion and interaction between TC molecules and biochar active sites dominate the process, and (ii) a slower phase, possibly controlled by intraparticle diffusion [16]. In the last 180 minutes (from 300 to 480 minutes), the kinetics show a slight decrease in TC removal, possibly due to partial desorption or surface interferences, such as multilayer formation or occupation of weaker active sites [17]. This behavior indicates that BioCH-M is an efficient adsorbent for TC removal, with stable and rapid performance in the first 300 minutes. However, to better understand the mechanisms involved, it is recommended that a fit to kinetic models such as pseudo-first-order, pseudo-second-order, or intraparticle diffusion models be performed.

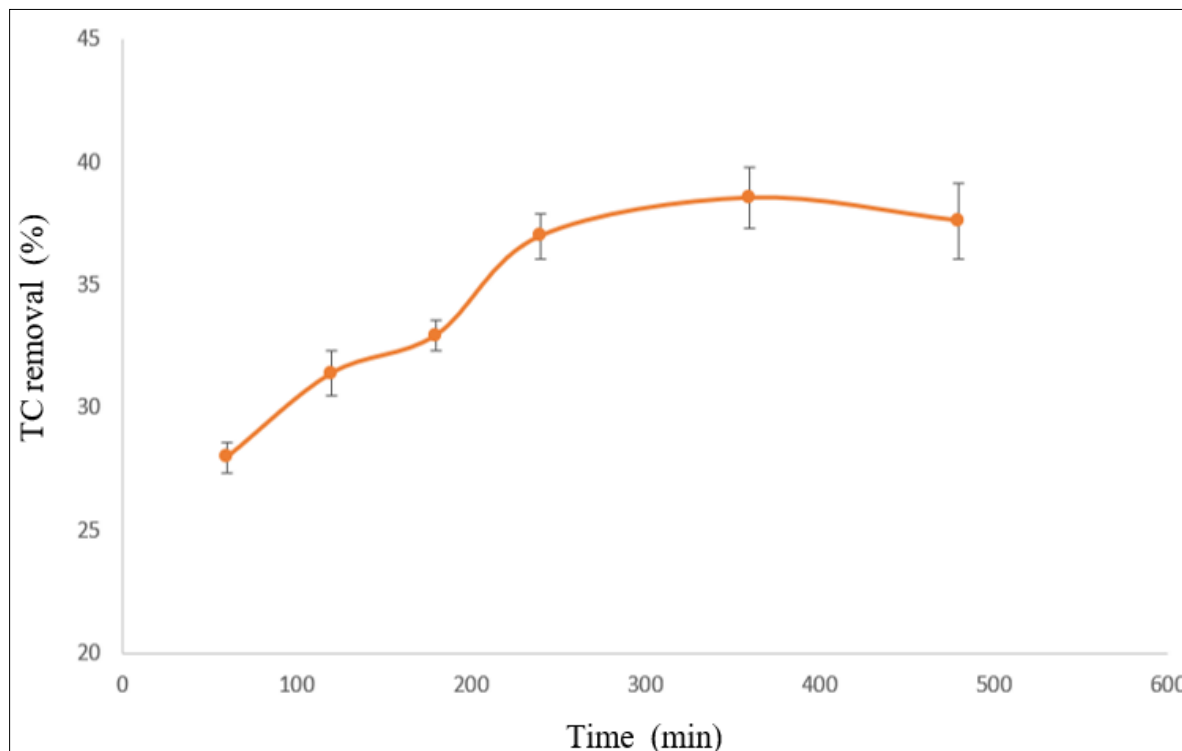


Fig. 4: Tetracycline Removal as a Function of Time using BioCH-M as Adsorbent.

Tetracycline adsorption kinetic data were analyzed using established empirical models: the Lagergren model, pseudo-second-order model, and the Elovich equation [18], [19], [20], through non-linear regression to derive the global reaction kinetic constants for each evaluated model. The kinetic data were previously transformed into the concentration of each ion in the sorbent (q_t) to enable fitting to these models using the subsequent equation:

$$q_t = (C_o - C_t)V/m \quad 1$$

Where C_o is the initial concentration of metal in the supernatant; C_t is the concentration of metal in the supernatant at time t , V is the volume of solution (L), m is the mass of the biosorbent (g), and q_t is the metal concentration in the biosorbent (mg/g). Table 1 shows each model's TC adsorption kinetic parameters and their correlation coefficients (R). The pseudo-first-order model, which assumes adsorption is proportional to the number of unoccupied sites on the adsorbent, has a moderate fit to the experimental data. However, the calculated q_e is significantly lower than the experimental values, suggesting that this model may need to capture the adsorption mechanism for tetracycline onto BioCH-M. The pseudo-second-order model, which typically reflects adsorption processes dominated by chemisorption, has a low R -value, suggesting that chemisorption may not be the predominant mechanism for tetracycline removal by BioCH-M. The Elovich model, which describes systems where the

adsorption rate decreases exponentially as surface coverage increases, has an excellent fit, suggesting that tetracycline adsorption occurs on a heterogeneous surface with varying activation energies.

The Elovich model reveals the heterogeneous nature of BioCH-M's surface, enhanced through NaOH modification. Studies show increased porosity and functional groups in NaOH-treated biochars, leading to better adsorption of organic pollutants [17]. Studies have shown faster adsorption rates and a better fit for the Elovich model. The low q_e values observed in the Elovich model are consistent with early-stage adsorption. The pseudo-first-order model moderately fits the data but underestimates adsorption capacity, while the pseudo-second-order model poorly represents the kinetics. BioCH-M's performance aligns with materials with heterogeneous adsorption but falls short in adsorption capacity compared to biochars with metal functionalization [21]. BioCH-M can be considered fast for adsorbing tetracycline, especially when compared to unmodified biochars. The rapid initial adsorption and the overall equilibrium time of about five hours are favorable, though not the fastest, compared to other adsorbents with higher surface areas or different modification treatments. Further modifications or optimization of the material (such as increasing surface area or incorporating additional functional groups) could potentially make BioCH-M even faster in terms of adsorption kinetics.

Table 1 Kinetic Parameters and Correlation Coefficients (R) of TC Adsorption by BioCH-M.

Model	Parameters	Correlation coefficient (R)
Lagergren	$K_L = 0.0148 \text{ min}^{-1}$ $q_e = 0.6441 \text{ mg/g}$	0.9334
Pseudo-second-order	$K_2 = 0.6838 \text{ g/mg.min}$ $q_e = 1.1502 \text{ mg/g}$	0.9187
Elovich	$a = 0.060 \text{ mg/g.min}$ $b = 7.956 \text{ g/mg}$	0.9852

D. Influence of pH on Adsorption

The pH of the solution affected the adsorption of tetracycline. Figure 5 illustrates the influence of solution pH on the removal of TC molecules when in contact with BioCH-M within a pH range of 2 to 8.

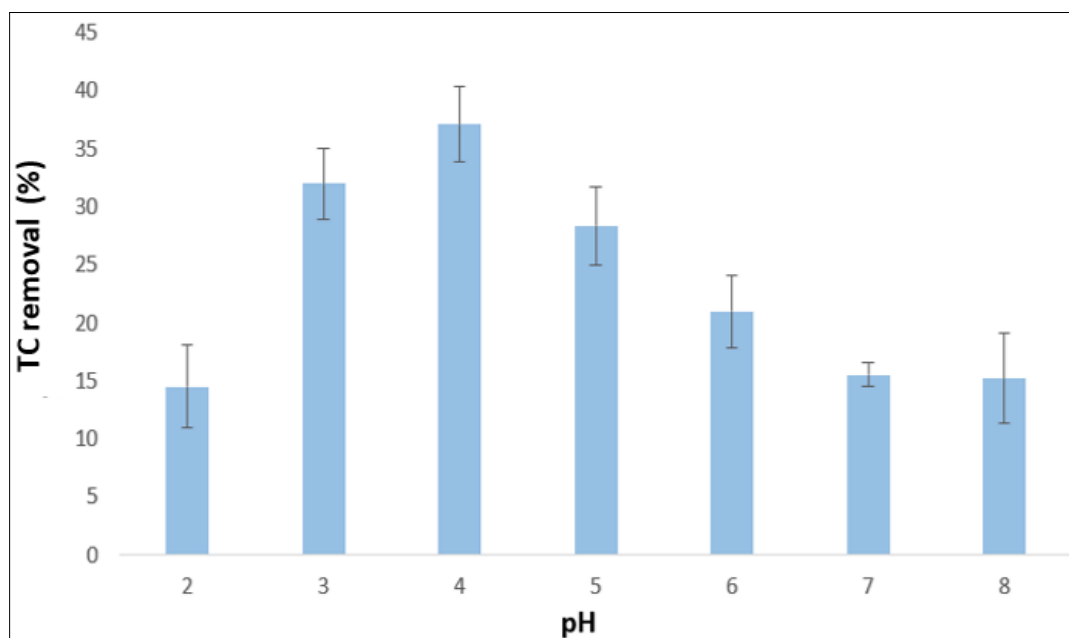


Fig. 5: Effect of solution's pH on TC removal using Bio-CH-M as adsorbent.

At pH 2, the TC removal is low, around 15%. At this very acidic pH, the positive charge of the biochar is high, reducing the affinity for TC molecules, which are neutral or slightly negative. At pH 3, the removal increases to about 35%. At this slightly acidic pH, the charge of the biochar starts to decrease, enhancing TC adsorption. pH 4 is the optimum value, with removal around 40%. The removal of tetracycline using biochar is more effective at slightly acidic pH values due to the interplay of several factors, including the surface charge of biochar, the chemical nature of tetracycline, and the adsorption mechanisms. At slightly acidic pH levels, the conditions are optimal for maximizing the interactions between biochar and tetracycline, leading to enhanced removal efficiency. This is primarily due to the electrostatic interactions, hydrogen bonding, and π - π interactions that are more favorable under these conditions [22], [23]. Biochar has an intermediate charge that maximizes the affinity for TC molecules. At pH 5 and 6, the removal decreases to about 25%. At this neutral pH, the charge of the biochar is lower, reducing the adsorption efficiency. The removal rate above pH 7 is around 20%. Under neutral and slightly alkaline conditions, the efficiency of biochar is considerably lower, around 20%. Tetracycline removal with biochar is low at

neutral and slightly alkaline pH values due to reduced electrostatic attraction and competing ions. The surface charge of biochar and tetracycline ionization state change, affecting adsorption efficiency. Competing ions like calcium and bicarbonate interfere with the process. Hydrogen bonding and π - π interactions are effective, but their effectiveness diminishes at higher pH levels [24]. The optimal pH for adsorption is around pH 3-4, where electrostatic attraction is stronger. In summary, TC removal using BioCH-M is most effective under slightly acidic conditions, with an optimum pH of 4. The efficiency decreases under very acidic, neutral, and slightly alkaline conditions. This may be due to the interaction between TC and biochar surfaces, which varies with the pH of the solution.

E. Adsorption Isotherms

The results obtained from the TC adsorption isotherms at different temperatures are shown in the graphs in Figure 6, where the concentration of TC retained in the modified biochar, q_e (mg TC/g BioCH-M), and C_e , the concentration of TC at equilibrium in the solution, C_e (mg TC/L), are plotted. The isotherm at 25°C (Figure 5a) shows a rapidly rising curve at first and then levels off as the equilibrium

concentration (C_e) increases. This behavior suggests a high initial affinity of the biochar for Tetracycline, followed by a saturation of the adsorption sites. The shape of this isotherm can be classified as an L-type isotherm according to the classification of Giles et al. [25]. L-type isotherms indicate a high affinity between the adsorbate and the adsorbent and a decrease in the availability of adsorption sites as these become saturated. The isotherm at 35°C also shows an ascending curve but with a less steep slope compared to the isotherm at 25°C. This suggests that the adsorption capacity of biochar decreases slightly as the temperature increases. The shape of this isotherm can also be classified as L-type, although with a lower affinity than the isotherm at 25°C. Finally, the isotherm

at 40°C shows a curve that initially rises, reaches a maximum, and then slightly decreases. This behavior may indicate partial desorption at higher temperatures, suggesting that adsorption is less favorable at 40°C. The shape of this isotherm can be classified as H-type, which is a variation of the L-type isotherm but with greater complexity due to the possible desorption at high temperatures. Therefore, it can be established that the adsorption equilibrium of Tetracycline in BioCH-M shows a high initial affinity that decreases with increasing temperature. These results are relevant to understanding how temperature affects the adsorption capacity of biochar and may help optimize treatment processes for water contaminated with Tetracycline.

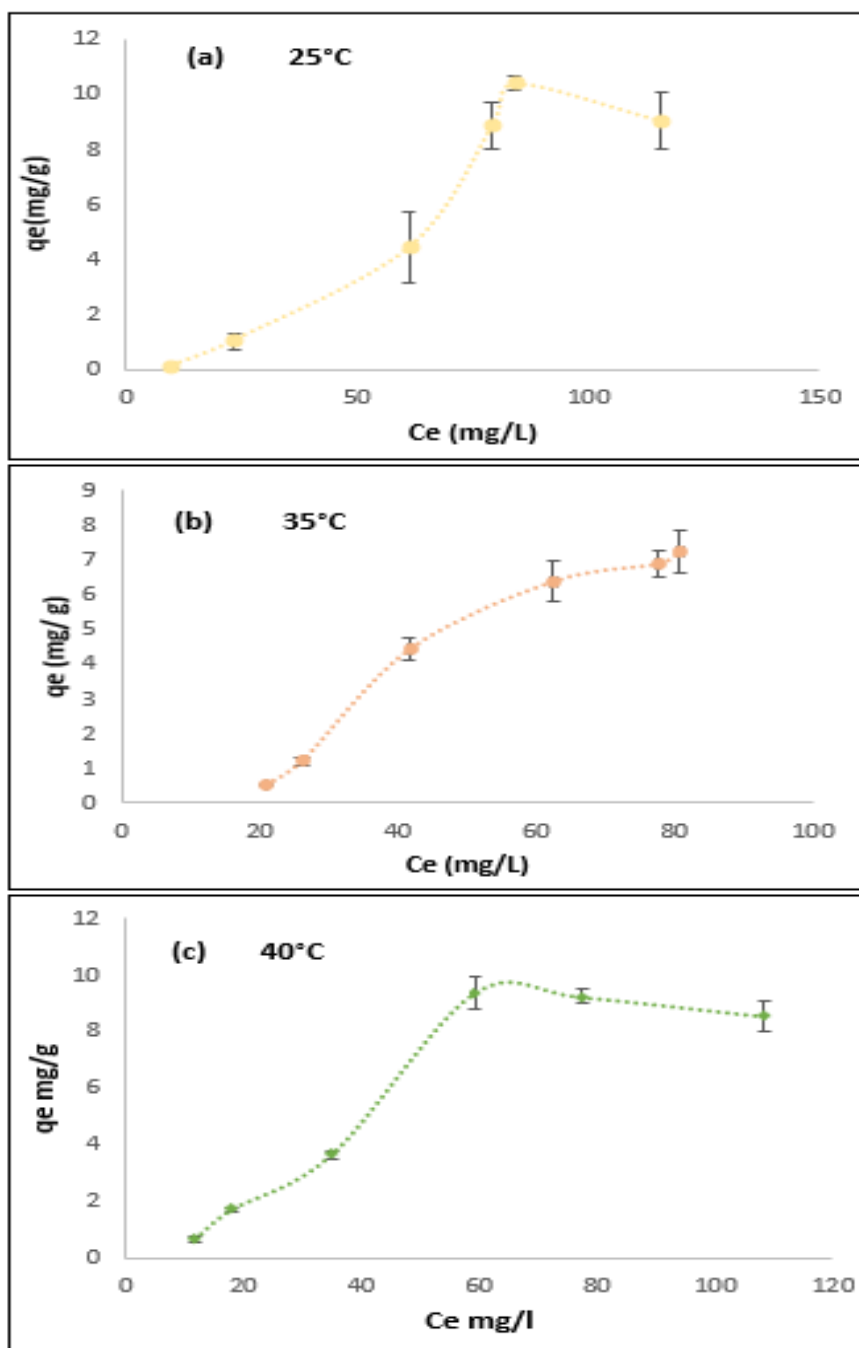


Fig. 6: Tetracycline Adsorption Isotherms using BioCH-M as Adsorbent at Different Temperatures.

Adsorption equilibrium studies allow for the determination of the maximum amount fixed on the adsorbent at a given solution concentration; therefore, the modeling consists of searching for a relationship between the theoretical q_e and C_e values that can correctly simulate and describe the isothermal data. As mentioned, this modeling was performed for the three TC adsorption isotherms, considering the well-known Freundlich, Langmuir, and Langmuir-Freundlich models. Table 2 shows the parameter values of these isotherm models through a non-linear regression analysis. The values of the correlation coefficient (R) for the three systems in each mathematical model are almost close to unity, so it can be considered that all the models can describe the TC adsorption

process using BioCH-M well. Langmuir isotherms show that biochar has a maximum theoretical adsorption capacity of 45.05 mg/g at 25 °C and a correlation coefficient of 0.920. At 35 °C, the adsorption capacity increases to 63.82 mg/g, and a correlation coefficient of 0.946. At 40 °C, the efficiency decreases due to temperature-induced desorption. Freundlich isotherms show that biochar has favorable adsorption at all temperatures, with values close to 1 suggesting favorable adsorption. Finally, Langmuir-Freundlich isotherms show that adsorption is less favored at 40 °C due to higher heterogeneity in adsorption sites. The study results are comparable to previous reports [15].

Table 2 Isotherm Parameters and Correlation Coefficients (R) of TC Adsorption by BioCH-M.

T (°C)	Langmuir			Freundlich			Langmuir-Freundlich			
	q_0	B	R	K	n	R	K	n	a	R
25	45.05	0.002	0.920	0.09	0.99	0.918	0.07	1.1	0.003	0.925
35	63.82	0.001	0.946	0.03	0.82	0.959	0.21	0.8	0.001	0.918
40	34.93	0.005	0.958	0.22	1.22	0.946	0.02	2.2	0.024	0.986

IV. CONCLUSIONS

This study on tetracycline removal using modified biochar (BioCH-M) derived from avocado peels has revealed significant findings that address the environmental risks and challenges in treating pharmaceutical contaminants in water. The results showed that BioCH-M has a porous morphology and an active surface facilitating interaction with tetracycline molecules. Analyses by FTIR and SEM confirmed that the modification of biochar improves its adsorption properties. The pH of the medium significantly influences the efficiency of the process, with slightly acidic being the most favorable for tetracycline removal. Mathematical models applied to the experimental data indicated that the adsorption follows a fast kinetic behavior, reaching equilibrium relatively quickly. This implies that BioCH-M is effective and rapidly removes tetracycline from water, which is advantageous for practical applications in wastewater treatment. The maximum adsorption capacity of tetracycline (TC) using alkaline-biochar modified (BioCH-M) is reported to be 45.05 mg/g at 25 °C, according to the Langmuir model analysis conducted in the study. This value is relatively high compared to similar reports. The study emphasizes that this high value reflects the effectiveness of BioCH-M as an adsorbent for removing tetracycline from aqueous solutions, highlighting its potential application in treating pharmaceutical contaminants in water systems.

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REFERENCES

- [1]. M. S. de Ilurdoz, J. J. Sadhwani, y J. V. Reboso, "Antibiotic removal processes from water & wastewater for the protection of the aquatic environment - a review", J. Water Process Eng., vol. 45, p. 102474, Feb. 2022, doi: 10.1016/j.jwpe.2021.102474.
- [2]. C. Peiris, S. R. Gunatilake, T. E. Mlsna, D. Mohan, y M. Vithanage, "Biochar based removal of antibiotic sulfonamides and tetracyclines in aquatic environments: A critical review", Bioresour. Technol., vol. 246, pp. 150-159, dic. 2017, doi: 10.1016/j.biortech.2017.07.150.
- [3]. S. A. Mousavi y H. Janjani, "Antibiotics adsorption from aqueous solutions using carbon nanotubes: a systematic review", Toxin Rev., vol. 39, n.o 2, pp. 87-98, abr. 2020, doi: 10.1080/15569543.2018.1483405.
- [4]. Y. Amangelsin, Y. Semenova, M. Dadar, M. Aljofan, y G. Björklund, "The Impact of Tetracycline Pollution on the Aquatic Environment and Removal Strategies", Antibiotics, vol. 12, n.o 3, Art. n.o 3, mar. 2023, doi: 10.3390/antibiotics12030440.
- [5]. R. Daghrir y P. Drogui, "Tetracycline antibiotics in the environment: a review", Environ. Chem. Lett., vol. 11, n.o 3, pp. 209-227, sep. 2013, doi: 10.1007/s10311-013-0404-8.
- [6]. G. Gopal, S. Ann Alex, N. Chandrasekaran, y A. Mukherjee, "A review on tetracycline removal from aqueous systems by advanced treatment techniques", RSC Adv., vol. 10, n.o 45, pp. 27081-27095, 2020, doi: 10.1039/D0RA04264A.

- [7]. M. S. Tunç y Ö. Hanay, "Removal of tetracycline antibiotic from aqueous solution using biosorbent", *Desalination Water Treat.*, vol. 261, pp. 308-321, jun. 2022, doi: 10.5004/dwt.2022.28525.
- [8]. K. S. D. Premarathna et al., "Clay-biochar composites for sorptive removal of tetracycline antibiotic in aqueous media", *J. Environ. Manage.*, vol. 238, pp. 315-322, May 2019, doi 10.1016/j.jenvman.2019.02.069.
- [9]. H. Meng et al., "Insight into the effect of lignocellulosic biomass source on the performance of biochar as persulfate activator for aqueous organic pollutants remediation: Epicarp and mesocarp of citrus peels as examples", *J. Hazard. Mater.*, vol. 399, p. 123043, nov. 2020, doi: 10.1016/j.jhazmat.2020.123043.
- [10]. E. Apaydın Varol and Ü. Mutlu, "TGA-FTIR Analysis of Biomass Samples Based on the Thermal Decomposition Behavior of Hemicellulose, Cellulose, and Lignin", *Energies*, vol. 16, n.o 9, Art. n.o 9, ene. 2023, doi: 10.3390/en16093674.
- [11]. A. Rahmat y M. Apriyanto, "Evaluation of the Characteristics of Avocado Seed Biochar at Various Pyrolysis Temperatures for Sustainable Waste Management", *Univers. J. Agric. Res.*, 2024, Accessed: November 2024. [Online]. Available at: <https://repository.unilak.ac.id/4204/>
- [12]. N. J. Salazar-López, M. L. Salmerón-Ruiz, J. A. Domínguez-Avila, M. A. Villegas-Ochoa, J. F. Ayala-Zavala, y G. A. González-Aguilar, "Phenolic compounds from 'Hass' avocado peel are retained in the indigestible fraction after an in vitro gastrointestinal digestion", *J. Food Meas. Charact.*, vol. 15, n.o 2, pp. 1982-1990, abr. 2021, doi: 10.1007/s11694-020-00794-6.
- [13]. X. Xu et al., "Enhanced adsorption capacity of antibiotics by calamus-biochar with phosphoric acid modification: Performance assessment and mechanism analysis", *J. Taiwan Inst. Chem. Eng.*, vol. 161, p. 105541, ago. 2024, doi: 10.1016/j.jtice.2024.105541.
- [14]. S. Jellali et al., "Investigations on Amoxicillin Removal from Aqueous Solutions by Novel Calcium-Rich Biochars: Adsorption Properties and Mechanisms Exploration", *Processes*, vol. 12, n.o 8, Art. n.o 8, ago. 2024, doi: 10.3390/pr12081552.
- [15]. Y. Dai, J. Li, y D. Shan, "Adsorption of tetracycline in aqueous solution by biochar derived from waste *Auricularia auricula* dregs", *Chemosphere*, vol. 238, p. 124432, ene. 2020, doi: 10.1016/j.chemosphere.2019.124432.
- [16]. Y. S. Ho y G. McKay, "Pseudo-second order model for sorption processes", *Process Biochem.*, vol. 34, n.o 5, pp. 451-465, jul. 1999, doi: 10.1016/S0032-9592(98)00112-5.
- [17]. K. Y. Foo y B. H. Hameed, "Insights into the modeling of adsorption isotherm systems", *Chem. Eng. J.*, vol. 156, n.o 1, pp. 2-10, ene. 2010, doi: 10.1016/j.cej.2009.09.013.
- [18]. Y. S. Ho, G. McKay, D. A. J. Wase, y C. F. Forster, "Study of the Sorption of Divalent Metal Ions onto Peat", *Adsorpt. Sci. Technol.*, vol. 18, n.o 7, Art. n.o 7, sep. 2000, doi: 10.1260/0263617001493693.
- [19]. M. J. D. Low, "Kinetics of Chemisorption of Gases on Solids.", ACS Publications. Accessed: August 2024. [online]. available at: <https://pubs.acs.org/doi/pdf/10.1021/cr60205a003>
- [20]. Lagergren, S. Zur theorie der sogenannten adsorption gelöster stoffe. *Bil. K. Svenska Venteskapsakad Handl* 1898; 24(4): 1-39.
- [21]. V.-T. Nguyen et al., "Efficient Heterogeneous Activation of Persulfate by Iron-Modified Biochar for Removal of Antibiotic from Aqueous Solution: A Case Study of Tetracycline Removal", *Catalysts*, vol. 9, n.o 1, Art. n.o 1, ene. 2019, doi: 10.3390/catal9010049.
- [22]. L. Zhang et al., "Simultaneous removal of U(VI) and tetracycline from aqueous solution by biochar-supported nano-hydroxyapatite: New insights into the role of biochar and interactions between pollutants", *Sep. Purif. Technol.*, vol. 345, p. 127303, oct. 2024, doi: 10.1016/j.seppur.2024.127303.
- [23]. L.-T.-T.-T. Hoang et al., "Utilization of dragon fruit (*Hylocereus undatus*) peel-derived biochar for the adsorptive removal of tetracycline from aqueous solution", *Int. J. Phytoremediation*, dic. 2024, Accessed: November 2024. [Online]. Available at: <https://www.tandfonline.com/doi/abs/10.1080/15226514.2024.2389471>
- [24]. Z. Zhang et al., "Novel sodium bicarbonate activation of cassava ethanol sludge derived biochar for removing tetracycline from aqueous solution: Performance assessment and mechanism insight", *Bioresour. Technol.*, vol. 330, p. 124949, jun. 2021, doi: 10.1016/j.biortech.2021.124949.
- [25]. C. H. Giles, D. Smith, y A. Huitson, "A general treatment and classification of the solute adsorption isotherm. I. Theoretical", *J. Colloid Interface Sci.*, vol. 47, n.o 3, Art. n.o 3, Jun. 1974, doi: 10.1016/0021-9797(74)90252-5.