JEE Journal of Ecological Engineering

Journal of Ecological Engineering, 2025, 26(9), 382–399
https://doi.org/10.12911/22998993/205417
ISSN 2299–8993, License CC-BY 4.0

Received: 2025.05.14
Accepted: 2025.06.14
Published: 2025.06.23

Rice husk biochar as a sustainable adsorbent for tetracycline removal from aqueous solution by using Taguchi design approach

Segundo Alberto Vásquez Llanos[1*], Lilibeth Lucia Sausa Burga[1], Danna Nicole Guevara Fernández[1], Marilín Nicoll Sánchez Purihuaman[2], Sebastian Huangal Scheineder[1], Carmen Rosa Carreño-Farfan[2], Magali Camila Vivas-Cuellar[3], Karina Rivadeneira Sipion[4], Juan Taumaturgo Medina Collana[5], Ada Patricia Barturén Quispe[1]

[1] Centro de Investigación Medio Ambiente y Desarrollo Sostenible, Facultad de Ingeniería Química e Industrias Alimentarias, Universidad Nacional Pedro Ruiz Gallo, Lambayeque, 14013, Perú
[2] Centro de Investigación Biodiversidad y Manejo Ecológico del Bosque Seco y Cultivos Agrícolas, Facultad de Ciencias Biológicas, Universidad Nacional Pedro Ruiz Gallo, Perú
[3] Grupo de investigación Biorrefinería, Facultad de Ingeniería Química y Textil, Universidad Nacional de Ingeniería, Lima, Perú
[4] Facultad Ingeniería Mecánica y Eléctrica, Universidad Tecnológica del Perú, Chiclayo, Perú
[5] Centro de Investigación de Ingeniería de Procesos de Tratamiento de Aguas, Facultad de Ingeniería Química, Universidad Nacional del Callao, Callao, Perú
* Corresponding author's e-mail: svasquezll@unprg.edu.pe

ABSTRACT

Tetracycline removal was evaluated in an aqueous solution with rice husk biochar using the Taguchi design with signal-to-noise ratio (S/N) under the 'Larger is better' condition. Carbonized biochar samples were prepared at 500, 625, and 750 °C (RHB500, RHB625, and RHB750, respectively) for 1 h. The variables investigated included carbonization temperature, contact time (1, 2.5, and 4 h), and biochar dosage (1, 10, and 20 g/L) at a controlled pH of 3. The results showed that the biochar yield decreased with a nonlinear trend from 39.60% to 29.36%, while the surface area of the BET increased from 12.75 to 231.04 m^2/g with increasing carbonization temperature from 500 to 750 °C. The adsorption capacity of rice husk biochar was optimal at 750 °C, a contact time of 4 hours, and a biochar dosage of 20 g/L, achieving a 100 % removal efficiency. Optimized conditions allowed 99.51% removal of pure tetracycline (50 mg/L) and 100% removal in a solution containing tap water and medical grade tetracycline. Kinetic analysis indicated that the adsorption process followed a pseudo-second order model, while the equilibrium data were best described by the Langmuir isotherm, with a maximum adsorption capacity of 6.009 mg/g at 25 °C. This suggests that the interaction between biochar and tetracycline is dominated by monolayer chemical reactions on homogeneous surfaces. These results underscore that RHB750 is an efficient, cost-effective, and easily accessible adsorbent and represents a viable and sustainable solution for the treatment of antibiotic contaminated water.

Keywords: rice husk, biomass, antibiotic, tetracycline, agricultural biochars, adsorption.

INTRODUCTION

Tetracycline (TC) belongs to a class of broad-spectrum antibiotics with phenanthrene cores that are not completely metabolized in humans or animals [Zhang et al., 2023]. It is a yellow antibiotic with spectral absorption in the range of 300 to 430 nm. It is partially absorbed into the gastrointestinal tract, with approximately 50% being excreted in its original form or as metabolites and released into the environment as a pollutant [Phakathi et al., 2022]. Studies have confirmed the persistence of TC and oxytetracycline in surface waters and sediments from marine culture ponds [Han et al., 2020]. Furthermore, chlortetracycline residues have been identified

in the water systems of fish farms, reaching concentrations of up to 87.4 ng/L, while oxytetracycline concentrations of 7.8 µg/kg and 10.08 mg/kg have been detected in trout muscle tissue and sediment, respectively [Vilca et al., 2021]. Furthermore, critical concentrations of up to 32 mg/L of oxytetracycline have been detected in wastewater from antibiotic production [Oberoi et al., 2019], and concentrations above 20 mg/L of TC have been found in the vicinity of some pharmaceutical factories [Gan et al., 2024]. Its exposure to the environment poses a significant risk to ecosystems and human health [Sun et al., 2024], making the removal of TC in wastewater a critical priority.

Various methods have been used to remove TC from aqueous matrices, including coagulation-flocculation-adsorption [Al-Kindi and Al-nasrawy, 2022], hydrodynamic cavitation degradation [Wang et al., 2022], advanced oxidation [Ari et al., 2024], enzyme degradation [Harguindeguy et al., 2024], adsorption-photocatalysis [Dou et al., 2024], microbial-algal biodegradation [Wang et al., 2025] and adsorption [Zeng et al., 2018]. Among these methods, adsorption is the most widely used method because of its high efficiency, low cost, and the absence of undesirable byproducts. Furthermore, it offers significant advantages such as simplicity, safety, cost-effectiveness, and effectiveness in removing pollutants at low concentrations [Yu et al., 2017]. Various adsorbents, nanoadsorbents and biochar have been used [Basheer, 2018]. Biochar is a carbonaceous material obtained by carbonizing lignocellulosic biomass under conditions of limited or no oxygen supply. The physicochemical properties of biochar vary depending on the thermochemical conversion process used (pyrolysis, hydrothermal carbonization, and gasification) and the intrinsic properties of the biomass used [Jindo et al., 2014]. Biochar is widely used in environmental applications due to its ability to immobilize or remove pollutants from soil, water, and air [Bushra and Remya, 2024].

Among the viable alternatives for the removal of TC in aqueous media, the use of biochar from rice husks (*Oryza sativa*), an abundant and inexpensive by-product of the agricultural industry, stands out [Atta et al., 2022]. This lignocellulosic residue, which represents approximately 20% of the net weight of rice, poses a significant environmental burden due to its low biodegradability and persistence in the environment, making its sustainable management difficult [Andrade et al., 2020]. Rice husk-derived biochar, with or without modifications, has been shown to be an efficient adsorbent material for the removal of emerging contaminants in aqueous systems, including metal cations, synthetic dyes, inorganic nutrients, and antibiotics, including TC [Bushra and Remya, 2024]. Despite advances in the use of biochar as a remediation technology, a knowledge gap remains regarding the simultaneous optimization of multiple operating parameters that affect the TC adsorption capacity when using nonfunctionalized adsorbents. Few studies systematically and statistically address the interaction between carbonization temperature, contact time, and adsorbent dose.

In this context, we propose to evaluate the efficiency of rice husk-derived biochar in TC adsorbing, analyzing the effects of carbonization temperature, contact time, and adsorbent dose using the Taguchi L9 experimental design with signal-to-noise ratio (S/N) under the 'Larger is better' condition. Using the optimal values, we evaluated the adsorption kinetics and isotherms. This approach will contribute to the development of a more efficient, sustainable and economically viable treatment technology for the removal of antibiotics from aqueous solutions.

MATERIALS AND METHODS

Materials

Rice husk was collected from the Gran Dorado mill in the Lambayeque region of Peru. The reagents used, NaOH (1 M) and H_2SO_4 (1 M), were of analytical grade. HPLC grade tetracycline (purity ≥ 99%) was purchased from Sigma-Aldrich, while commercially available pharmaceutical tetracycline capsules were obtained from a local pharmacy. For the pH analysis, distilled water, ultrapure water (18.2 MΩ.cm) at 25 °C, and tap water were used to prepare pure tetracycline solutions and solutions with the powder contents extracted from commercially available 500 mg pharmaceutical capsules, respectively.

Characterization of rice husk and biochar

The previously washed and dried rice husks were crushed and sieved in a domestic mill (Corona L12104) to obtain retained fractions in 60 and 100 mesh sizes. The content of ash and volatile

matter were determined using ASTM D-3174 and ASTM D-3175 methods, respectively, and the fixed carbon content was determined by difference. Biochar was washed three times with distilled water (1:10, w/v), with a 30 minute rest period between washes to remove soluble contaminants that could discolor treated water [Rodríguez et al., 2020]. They were then dried for 22 h at 80 °C [Thairattananon et al., 2024], manually crushed with a mortar and pestle, and again the material was retained in 60 and 100 mesh sieves. The approximate analysis was made in triplicate. The BET surface area and total pore volume were analyzed using a Micromeritics Autochem II 2920 analyzer by nitrogen adsorption at -180 °C. The samples were degassed at 100 °C for 30 minutes before analysis. The surface area was determined using the single-point method at a relative pressure of 0.3, while the total pore volume was determined from the volume of adsorbed nitrogen at a relative pressure of 0.97.

Biochar preparation

Rice husks (RH) were washed twice with tap water to remove surface residues and dried for 24 h at 105 °C in a circulating air oven (Binder, model FD 115). Subsequently, 40 g of dry RH was placed in a 300 ml porcelain crucible, the contents were leveled, covered with aluminum foil, and the corresponding lid was placed to ensure an airtight seal and generate a low-oxygen environment. Carbonization was carried out in a muffle furnace (Thermolyne Eurotherm, 2116) at temperatures of 500 °C, 625 °C, and 750 °C, with a residence time of 1 h after reaching the carbonization temperature. After carbonization, the samples were allowed to cool in the muffle furnace for 24 h until they reached room temperature (Figure 1). The resulting biochars were weighed, labeled RHB500, RHB625, and RHB750 according to their carbonization temperature, and stored in zip-lock bags in a desiccator for later analysis. To evaluate the effect of carbonization temperature on biochar yield (five replicates for each temperature), a one-way analysis of variance (ANOVA) with significance level and Tukey's post hoc test were applied. Additionally, a nonlinear regression analysis was performed using OriginPro software to model this effect. The R^2 value was considered as a goodness-of-fit criterion, and a 95% confidence level was used to validate the nonlinear model.

Experimental design

The experimental design was carried out according to the Taguchi approach, with the aim of determining the optimal operating conditions to evaluate the influence of the selected factors on the efficiency of tetracycline removal. The orthogonal matrix L9 (3^3) with three factors and three levels was used to evaluate the control factors and their interactions. The parameters are presented in Table 1.

The experimental results were evaluated using analysis of variance with a 95% confidence level to determine the statistical significance of each parameter and its contribution to the process. The percentage contribution of each experimental variable was calculated from the analysis. Furthermore, the influence of the experimental parameters was assessed by analyzing the signal-to-noise ratio (S/N) under the condition 'Larger is better' according to Equation 1. Experimental data processing was performed using Minitab® 21.1.

$$(S/N)_{j,k} = -10\log\left(\frac{1}{n}\sum\frac{1}{y^2}\right) \quad (1)$$

where: n is the number of repetitions of level k in factors j and y is the output response.

Figure 1. Preparation of biochar derived from rice husks

Table 1. Process parameter values at three different levels

Control factor	Levels			
	1	2	3	Units
Carbonization temperature	500	625	750	°C
Contact time	1	2.5	4	min
Biochar dose	1	10	20	g/L

Spectrophotometric calibration curve

Two spectrophotometric calibration curves were developed for the TC measurement, using an identical procedure in both cases. For each curve, a 100 mg/L TC stock solution was prepared using ultrapure water; one was derived from HPLC grade TC and the other consisted of the powder contents extracted from commercially available 500 mg pharmaceutical capsules. Standard solutions with concentrations of 20, 40, 60, and 80 mg/L were prepared from these stock solutions. Absorbance measurements were performed at a wavelength of 360 nm [Zhang et al., 2023] on a Thermo Scientific GENESYS 30 visible spectrophotometer. Each curve was used to determine the residual TC concentration, ensuring traceability to the source of compound.

Batch adsorption tests

Batch adsorption experiments were performed in an aqueous TC solution containing 50 mg/L in ultrapure water. 100 mL of this solution was added to each 250 mL flask, and 1, 10, or 20 g/L of the previously prepared biochars (RHB500, RHB625, and RHB750) were added. The pH of the mixture was adjusted to 3 using 1 M H_2SO_4 or NaOH solutions [Jeganathan et al., 2024]. This value was selected because TC exhibits cationic speciation in acidic conditions, which improves the interaction with biochar [Jang et al., 2018]. Additionally, low pH helps prevent removal efficiency losses due to changes in adsorbent surface charge at higher pH levels [Fan et al., 2018]. The samples were shaken at 150 rpm and 25 °C in an orbital incubator (EUROTECH FS-70B) for contact times of 1, 2.5, and 4, according to the experimental design matrix (Table 3).

To determine TC removal efficiency and adsorption capacity, 10 ml of supernatant was extracted, filtered with a 0.45 µm syringe filter and the remaining TC concentration was analyzed using a spectrophotometer. Each test was carried out in triplicate and the data was expressed as mean ± standard deviation. The adsorption capacity (q, mg/g) and removal efficiency (R, %) were calculated according to Equation 2 and 3, respectively.

$$q = \frac{V(C_o - C_t)}{m} \quad (2)$$

$$R = \frac{(C_o - C_t)}{C_o} \times 100\% \quad (3)$$

where: C_o and C_t (mg/L): initial concentration and concentration at time t, respectively; V (L): solution volume and m (g): dose of biochar.

With the optimal parameters obtained with the Taguchi experimental design, the TC removal efficiency was validated using a solution prepared with tap water and the powder content of commercial 500 mg pharmaceutical capsules at a concentration of 50 mg/L, maintaining the experimental conditions previously established for the HPLC grade compound.

Adsorption kinetics tests

Adsorption kinetics were evaluated by adding 20 g/L RHB750 to 100 mL of TC solution (50 mg/L, pH = 3) in a 250 ml flask. All experiments were carried out in triplicate. The mixtures were shaken at 150 rpm and 25 °C in an orbital incubator. At intervals of 1, 5, 10, 15, 20, 30, 40, 50, 60, 75, 120, 150, 240, and 480 minutes, 10 mL of supernatant aliquots were removed, filtered with 0.45 µm syringe filters, and the remaining TC concentration was measured in a spectrophotometer at an absorption length of 360 nm. To describe the adsorption mechanism, the experimental data were fitted with pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models according to Equation 4 and Equation 5, respectively. The

kinetic parameters of each model were determined by linear regression using the OriginPro software. The fitting was validated using the determination coefficient (R^2) and the analysis of variance with a 95% confidence level.

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where: q_e (mg/g) is the adsorption at equilibrium, q_t (mg/g) is the adsorption at time t (min), k_1 is the PFO rate constant (min^{-1}), and k_2 is the PSO rate constant (g/mg.min).

Adsorption isotherm tests

To investigate adsorption equilibrium, TC solutions were prepared with initial concentrations of 10, 30, 50, 70, and 100 mg/L, keeping volume of the solution (25 mL), pH (3), the dose of RHB750 biochar (20 g/L), and temperature (25 °C) constant. The mixture, contained in 100 mL flasks, was stirred for 8 hours at 25 °C in an orbital incubator. Aliquots of 10 mL of the supernatant were taken, filtered with 0.45 µm syringe filters, and the residual TC concentration was measured at an absorption length of 360 nm in the spectrophotometer. The experimental data were fitted with the Langmuir and Freundlich models according to Equation 6 and Equation 7, respectively. The isothermal parameters of each model were determined by linear regression using the OriginPro software. The fitting was validated using the determination coefficient (R^2) and the analysis of variance with a 95% confidence level.

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} K_L} + \frac{C_e}{Q_{max}} \quad (6)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

where: q_e (mg/g) is the adsorption at equilibrium, C_e (mg/L) is the equilibrium concentration, K_L (L/mg) is the Langmuir constant, Q_{max} (mg/g) is the maximum adsorption capacity, K_F is the Freundlich constant, and n is the sorption capacity and intensity.

RESULTS AND DISCUSSION

Physicochemical characterization of rice husk and rice husk-derived biochar

Table 2 presents the results of the physicochemical characterization of rice husk (RH) and rice husk-derived biochars (RHB) obtained at the carbonization temperature of 500 °C, 625 °C and 750 °C.

The progressive carbonization of RH resulted in a significant decrease in volatile matter, from 76.55% in RH to 9.0% in RHB750. This substantial decrease is attributed to the thermal decomposition of the lignocellulosic structure as the carbonization temperature increases. This behavior is consistent with the characteristic volatilization profiles of agricultural waste subjected to pyrolysis [Jindo et al., 2014; J. Sun et al., 2017].

The ash content increased from 15.66% for RH to 45.54% for RHB750. Thermal increase during carbonization resulted in a higher concentration of inorganic and organic compounds that did not volatilize during the thermal decomposition of RH [Sukarta et al., 2025]. Furthermore, the high silica content in RH, which remains in a solid state during carbonization, produces biochar with a high ash content [Jia et al., 2018]. Previous studies reported an increase in RHB ash content of 64.19% and 76.2% by increasing the pyrolysis temperature from 300 to 700 °C with a residence time of 3 h [Jia et al., 2018] and between 27.9% and 38.5% by increasing the temperature from 400 to 600 °C with a residence time of 1 h [Campos et al., 2020]. The increase in fixed carbon content to 45% in RHB, without significant differences between the three carbonization temperatures evaluated, represents an improvement in the thermal stability of carbon compared to 7.79% in RH. These values significantly exceed those reported in previous studies, where between 20.7% and 21.7% fixed carbon was generated in RHB between 400 and 600 °C for 1 h [Campos et al., 2020]. The increase in fixed carbon content promotes stabilization of the carbon matrix and a larger specific surface area, which increases the active adsorption sites and improves the adsorption capacity of the TC [Jeganathan et al., 2024].

The efficiency of biochar as an adsorption material correlates positively with its specific surface area, as this property enhances the exposure of functional sites and promotes interaction mechanisms such as hydrogen bonding, van der

Table 2. Characterization of rice husk and rice husk-derived biochar

Parameters	Sample			
	Rice husk	RHB500	RHB625	RHB750
Volatile matter, %	76.55 ± 0.32	14.17 ± 0.11	10.51 ± 0.46	9.00 ± 0.12
Ash, %	15.66 ± 0.04	41.46 ± 0.26	44.18 ± 0.03	45.54 ± 0.14
Fixed carbon, %	7.79 ± 0.27	44.37 ± 0.37	45.31 ± 0.49	45.46 ± 0.26
BET surface area, m^2/g	na	12.75	84.11	231.04
Total pore volume, cm^3/g	na	0.0064	0.042	0.12

Note: RHB: rice husk biochars; 500: means the carbonization temperature; na: not analyzed.

Waals forces, and π-π interactions [Saghir et al., 2022]. These interactions are based on the presence of functional groups such as hydroxyl, carbonyl and carboxyl, which provide the necessary chemical sites to form specific compounds with pollutant molecules, thus increasing the retention capacity of newly formed compounds in aqueous systems [Jiang et al., 2024; Saghir et al., 2022]. The specific surface area of the RHB increased from 12.75 m^2/g (500 °C) to 231.04 m^2/g (750 °C), an increase of approximately 18 times. Parallelly, the total volume of the pores increased from 0.0064 cm^3/g to 0.12 cm^3/g. These textural changes are attributed to the release of volatile substances such as hemicelluloses and cellulose, as well as the formation of channel structures during pyrolysis [Zeng et al., 2018]. Furthermore, increasing the carbonization temperature leads to a reorganization of the carbon network, which in turn increases the surface area and porosity, thus significantly improving the adsorption capacity [Alghyamah et al., 2021; Asadi et al., 2021].

In this context, the results suggest that higher carbonization temperatures (750 °C) are preferable for the production of biochar with optimized physicochemical properties for tetracycline adsorption, outperforming the RHB obtained at 500 °C. Several studies have reported the influence of pyrolysis temperature on the textural properties of biochar. Biochar treated at higher temperatures exhibits a larger specific surface area, which means increased availability of adsorption sites. This effect, which correlates with the increase in total pore volume, enhances its potential for adsorption applications [Zhang et al., 2024]. Increasing the temperature from 300 to 700 °C for 3 h increased the surface area of RHB from 78.401 to 377.717 m^2/g, achieving a Cd^{+2} removal of 96.12% for samples pyrolyzed at 700 °C [Jia et al., 2018]. Similarly, another study reported an increase in surface area from 2.02 to 211.76 m^2/g at similar temperatures and a residence time of 2 h, achieving an adsorption capacity of 80.9 mg/g for TC with RHB prepared at 700 °C [Zeng et al., 2018]. The pores of RHB further improved at pyrolysis temperatures up to 900 °C, reaching an area of 274.6 m^2/g and a porosity of 0.315, which was attributed to the progressive thermal decomposition and mass loss of the biochar [Tsai et al., 2021].

The progressive transformation of the physicochemical and textural properties observed in biochars highlights the importance of optimizing the pyrolysis conditions to obtain materials with suitable characteristics for specific applications in the treatment of water contaminated with antibiotics. Increasing the carbonization temperature significantly modifies the structural and functional properties of biochars, affecting their TC removal capacity through mechanisms including surface adsorption, π-π interactions, and hydrophobic attraction [Fan et al., 2018].

Effect of carbonization temperature on the yield of rice husk biochar (RHB)

The yield was calculated as the proportion of RHB mass in relation to the original mass of rice husk (RH) supplied in each experiment, expressed as a percentage and on a dry basis. As the carbonization temperature increased to 500, 625, and 750 °C, the RHB yield decreased to 39.60 ± 0.87%, 35.70 ± 0.21%, and 29.36 ± 0.83%, respectively. A one-way analysis of variance (ANOVA) confirmed that the observed differences between the temperatures tested were statistically significant ($p < 0.05$), and Tukey's post hoc test supports the assumption that each temperature represents a different group in terms of performance (Figure 2a). The decrease in RHB yield with increasing carbonization temperature is attributed to the intensification of thermal degradation of RH, which promotes the conversion

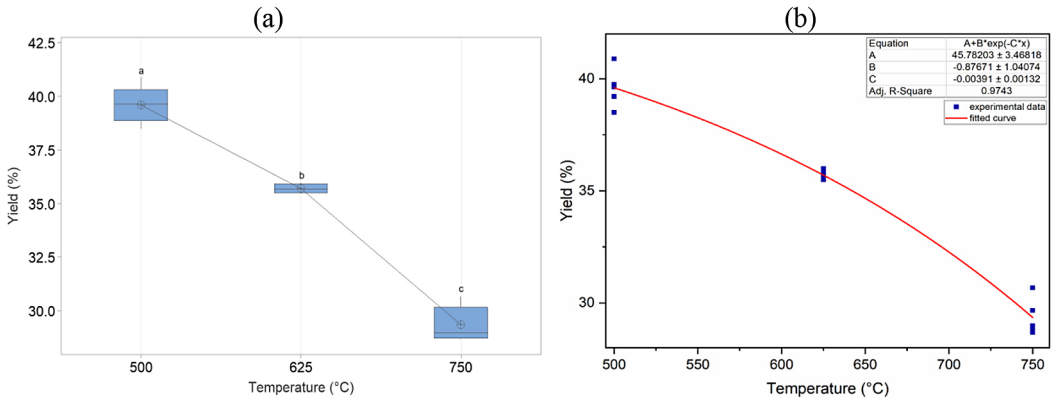

Figure 2. Rice husk biochar yield as a function of temperature; (a) one-way ANOVA, $p < 0.05$; (b) nonlinear regression curve

of volatile compounds into non-condensable gases and liquids of low molecular weight, resulting in a decrease in RHB yield from 55% to 35% when the pyrolysis temperature increases from 300 to 700 °C [Nwajiaku et al., 2018]. Since RH contains lignin and cellulose, carbonization at 600 °C for 2 h resulted in a RHB yield of 27.16% due to progressive thermal degradation of structural biopolymers and reduction of hydrogen and oxygen through thermal cracking reactions, leading to the release of volatile organic compounds and CO_2 [Aziz et al., 2023].

The quantitative relationship between the RHB yield and the carbonization temperature was analyzed using a nonlinear regression based on an exponential model that adequately describes this behavior ($R^2 = 0.9743$, $p < 0.05$), indicating a robust and reliable agreement between the experimental data and the fitted model (Figure 2b). For various lignocellulosic residues such as oak, pine, sugarcane, and peanut shells, an exponential yield decline was observed with increasing temperature (350 and 900 °C, 1 h residence time), with determination coefficients (R^2) exceeding 0.96 [Zhang et al., 2017]. The same trend was observed for the residues of the twig, leaf and pecan shell, with highly significant exponential decays ($R^2 > 0.99$) as the temperature increased between 300 and 600 °C during a residence time of 1 h [Liu et al., 2023]. For rice straw, they reported a decrease in biochar yield from 51.36% to 32.75% by increasing the pyrolysis temperature from 300 to 600 °C for a residence time of 1 h, observing an R^2 value of 0.85 for the logarithmic fit [Zhang et al., 2020]. In the case of rice husks, a linear decrease in biochar yield was reported from 75.3% to 32.6% with increasing pyrolysis temperature between 250 and 350 °C [Jeganathan et al., 2024].

These findings confirm the results and highlight the inverse correlation between carbonization temperature and biochar yield, with thermal enhancement favoring improved structural and functional properties for environmental applications, particularly in the adsorption of organic pollutants. Furthermore, the obtained nonlinear regression model, compared with previous studies, underscores that biochar yield is an important parameter for industrial production and that fitted regression models provide a useful reference for carbonization optimization [Liu et al., 2023].

Factor analysis using Taguchi design and S/N ratio

To determine the optimal conditions for maximizing TC adsorption efficiency and evaluate the relative influence of each operating parameter, the Taguchi experimental design was applied. Three factors were considered: the carbonization temperature of the RH (500, 625, and 750 °C), the contact time (1, 2.5, and 4 h), and the dose of RHB (1, 10, and 20 g/L). The TC removal efficiency achieved in each experimental combination and the corresponding signal-to-noise ratio (S/N) values are listed in Table 3. The 'Larger is better' criterion was used for the analysis, as the goal was to maximize process efficiency. The S/N values provide an integrated measure of the average system performance and its robustness (signal) against experimental disturbances (noise).

Operating conditions that combined a carbonization temperature of 750 °C, a contact time of 1 h and a dose of 20 g/L of RHB resulted in the

Table 3. Signal-to-Noise Ratio (S/N) for tetracycline adsorption

Experiment	Factors			Results	
	Carbonization temperature (°C)	Contact time (h)	RHB dose (g/L)	Efficiency (%)	S/N
1	500	1	1	2.40	7.59
2	500	2.5	10	33.62	30.53
3	500	4	20	57.32	35.17
4	625	1	10	36.11	31.15
5	625	2.5	20	71.58	37.10
6	625	4	1	13.13	22.37
7	750	1	20	97.83	39.81
8	750	2.5	1	19.35	25.73
9	750	4	10	92.91	39.36

highest TC removal efficiency of 97.83% and also recorded the highest S/N ratio of 39.81. On the contrary, the combination of 500 °C, 1 h of contact and a dose of 1 g/L of RHB resulted in the lowest efficiency of 2.40% and the lowest S/N ratio of 7.59. This wide range of S/N ratio values demonstrates the high sensitivity of the process to operating conditions and underscores the importance of proper optimization to ensure both system performance and stability. The main effect analysis of the S/N ratios for each factor level, shown in Figure 3, shows a positive influence of all three factors, suggesting that higher carbonation temperatures, contact times and adsorbent doses are associated with higher efficiency and greater stability. The strongest effect is observed for the adsorbent dose, where the slope is significantly steeper, confirming that this parameter has the greatest operational weight in the system. Therefore, this behavior reflects a robust process when the parameters are operated at their highest levels, especially with regard to the adsorbent dose.

Table 4 quantitatively confirms these observations, classifying the factors according to their impact on the process. RHB dose (factor C) showed the greatest effect, with response values between 18.56 and 37.36, followed by carbonization temperature (factor A) with response values between 24.43 and 34.97, while contact time (factor B) showed the least effect, ranging from 26.18 to 32.30.

The dose of RHB (factor C) was found to be the statistically significant factor ($p < 0.05$) in the TC adsorption process, contributing 70.78% to the total variation. This result supports the experimental and graphical analysis and confirms the critical importance of this factor for the efficient removal of TC. On the contrary, the carbonization temperature (factor A) contributed 19.87% to the total variation, with $p = 0.085$. Although this value did not reach the 95% confidence level, the magnitude of its effect suggests that it could be considered a relevant factor in studies with a greater number of replicates or greater statistical power. In fact, its influence on the physicochemical structure of RHB could be crucial for future process design, especially in optimized adsorbent production, and its optimization is key to maximizing material performance without unnecessary energy costs. Contact time (factor B) was the least influential factor, with a contribution of 7.51% ($p = 0.197$), indicating a nonsignificant effect in the evaluated time interval. Nevertheless, this parameter remains relevant from an operational and kinetic perspective, as it defines the time required to reach adsorption equilibrium. The experimental error was 1.84%, reflecting the reproducibility and precision of the experimental design and the reliability of the data obtained. The study demonstrated that operational factors have a heterogeneous influence on the removal efficiency of TC by RHB.

Effect of biochar dose on adsorption

Increasing the biochar dose (RHB750) from 1 to 20 g/L significantly increased the adsorption efficiency, reaching a maximum removal of 97.83% under favorable conditions. This behavior can be explained by the larger number of available active sites as the adsorbent mass increases, resulting in a larger contact area between the adsorbent and the TC molecules present in the solution. In particular, it is observed that although removal efficiency continues to increase with increasing doses, this improvement becomes less significant

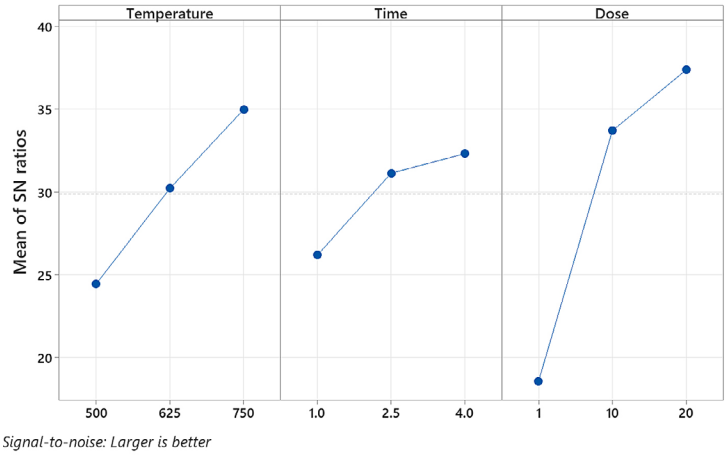

Figure 3. Main effects plot (data mean) for S/N ratios

Table 4. Response table for signal-to-noise (S/N) ratios

Factors		Response (average) value			Rank
		1	2	3	
A	Carbonization temperature (°C)	24.43	30.21	34.97	2
B	Contact time (h)	26.18	31.12	32.30	3
C	RHB dose (g/L)	18.56	33.68	37.36	1

Note: The classification of factors according to their range of influence (C > A > B) is consistent with the results of the ANOVA analysis (Table 5).

Table 5. ANOVA table for the output response (TC removal)

Source	Degree of freedom	Sum of squares	Mean square	F-Value	P-Value	Contribution (%)
A	2	167.09	83.546	10.78	0.085	19.87
B	2	63.13	31.566	4.07	0.197	7.51
C	2	595.19	297.597	38.41	0.025	70.78
Error	2	15.50	7.748			1.84
Total	8	840.91				100.00

beyond a certain threshold, suggesting a possible effect of saturation of the usable surface or particle aggregation, which could hinder access to the innermost active sites [Wang et al., 2023]. This phenomenon has been documented in various studies in which increasing the initial dose results in a significant improvement in removal, but at high doses the efficiency stabilizes or even decreases slightly due to the formation of aggregates that block part of the adsorbent surface, thus reducing its effective availability [Al-Kindi and Alnasrawy, 2022]. Similarly, in oxytetracycline adsorption systems with rice husk ash, increasing the dose increased the removal percentage, directly due to the larger number of adsorption sites, although efficiency remained constant above a critical value (~1.6 g), indicating a saturation point [Andrade et al., 2020]. Similarly, in the adsorption of several antibiotics in biochar, an increase in efficiency was observed up to 1.2 g/L, followed by equilibrium, which was attributed to saturation of the active sites at low doses and surface shielding caused by agglomeration at high doses [Zeng et al., 2018].

The results obtained are consistent with the scientific literature and confirm that increasing the dose of adsorbent improves removal efficiency up to an optimal point. Subsequently, structural limitations of the material, as well as saturation or agglomeration effects, prevent further improvements. This underscores the importance of carefully optimizing the adsorbent dose, considering

both the overall yield and specific efficiency per gram, to ensure a technically effective and economically viable adsorption process.

Effect of carbonization temperature on adsorption

Experimentally, an increase in removal efficiency was observed from 2.40% at 500 °C to 97.83% at 750 °C, supported by the increase in average signal-to-noise ratio values from 24.43 to 34.97. This behavior suggests that carbonization at higher temperatures favors the development of a biochar with a larger surface area and a greater number of active sites available for interaction with TC molecules, improving the adsorption process [Jeganathan et al., 2024]. Furthermore, the aromatic condensation of biochar produced at elevated temperatures has been reported to be a crucial component of process efficiency, contributing to greater structural stability and adsorption capacity [Zhang et al., 2024]. Similar behaviors have been documented for biochars from rice husks, sawdust, and municipal biowaste pyrolyzed at 700 °C. These exhibited more aromatic, polar, and hydrophobic structures, which favored the adsorption of antibiotics such as moxifloxacin and ofloxacin [Akhtar et al., 2021]. In highly carbonized biochars, TC adsorption occurs predominantly through intermolecular interactions, as the more developed carbon clusters have a higher density of active sites [Zhang et al., 2024]. The same effect was observed for the adsorption of other antibiotics, such as tetracycline hydrochloride, doxycycline and ciprofloxacin, whose removal increased significantly when using biochar produced at 700 °C compared to biochar produced at 300 °C or 500 °C [Zeng et al., 2018]. Consistently, a removal efficiency of nearly 91% was reported for carbonized rice straw biochar at 700 °C, while the same material barely reached 45% at 300 °C, confirming the positive effect of carbonization temperature on the efficiency of the adsorption process [Wang et al., 2017].

Effect of contact time on adsorption

The experimental results showed that increasing the interaction time between the contaminated solution and biochar from 1 to 4 h also increased the efficiency of TC removal, suggesting that the adsorption process is more intensive in the initial stages. This behavior is typical for systems in which high-energy, easily accessible active sites are rapidly occupied, resulting in an initial phase of high adsorption rate, followed by a slower phase as the system approaches equilibrium. When these sites are saturated, the adsorption stabilizes and the removal capacity tends to remain constant, reflected in a lower removal slope after 2.5 h of contact. This pattern has also been described in similar systems, where the rapid drop in antibiotic concentration during the first minutes is attributed to the high availability of free sites, while over longer periods the adsorption rate decreases due to the progressive surface saturation and repulsion between adsorbed molecules and those in the solution [Andrade et al., 2020]. This rapid process can be further explained by the abundance of active sites on the biochar surface in the early stages, as well as by the concentration gradient between the solution and the adsorbent, which acts as a driving force for the transport of TC molecules to the active surface of the material, where they are fixed through physicochemical interactions [Zhao et al., 2024]. Other studies have consistently shown that the higher adsorption rate in the initial stages is directly related to the availability of free sites in biochar, while between 90 and 120 minutes, the adsorption rate tends to stabilize due to the reduction of these active sites, thus reaching the equilibrium of the system [Wang et al., 2023].

Adsorption kinetics study

The kinetic curves show that the adsorption was rapid during the first 30 minutes, moderate during the following 30 minutes, and slower during the following hours. After approximately 60 minutes, equilibrium was reached, with a removal efficiency of 97.83% and an adsorption capacity of 2.5 mg/g, as shown in the Figure 4a and the parameters summarized in Table 6.

The pseudo-second-order (PSO) kinetic model better fitted the experimental data, with a coefficient of determination of $R^2 = 0.9988$ (Figure 4c), than the pseudo-first-order (PFO) model, which had a coefficient of determination of $R^2 = 0.9042$ (Figure 4b). This behavior suggests that the adsorption process is predominantly governed by chemisorption mechanisms, where the rate is controlled by chemical interactions between the active sites of the biochar and the TC molecules. This interpretation is consistent with a study that observed strong agreement of the PSO model with processes dominated by chemical reactions

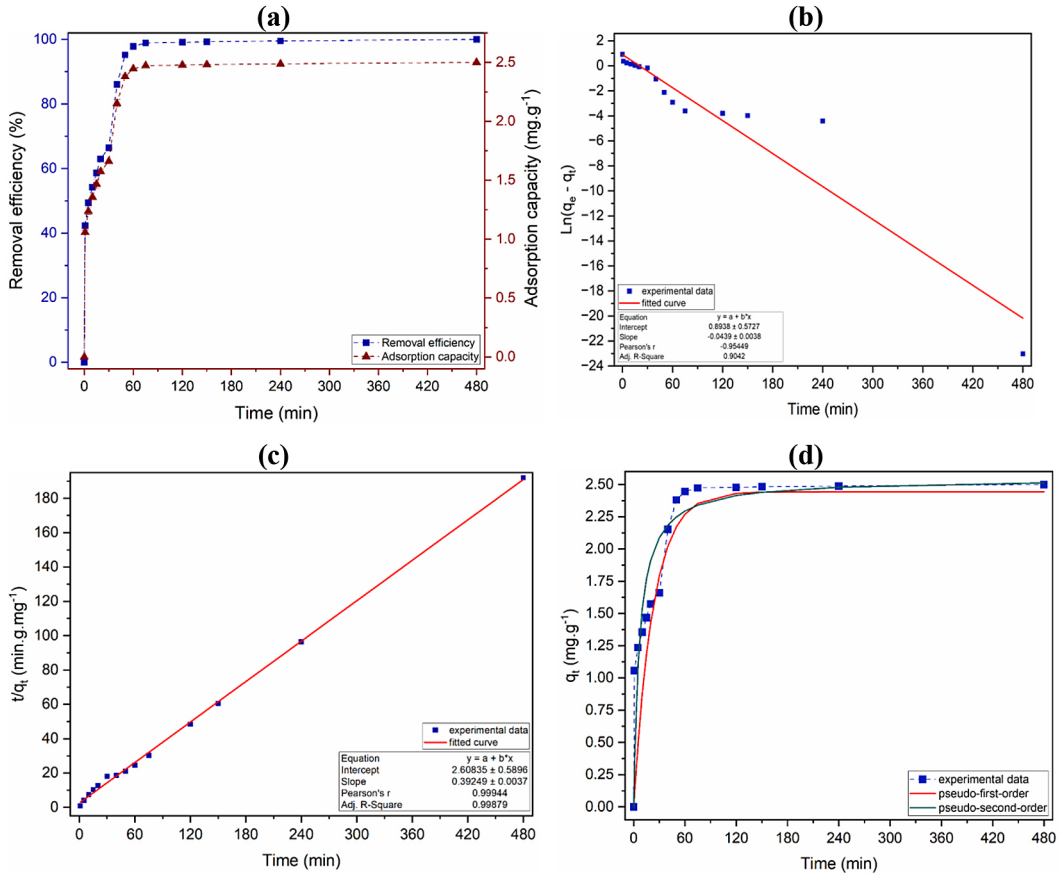

Figure 4. Kinetic for adsorption of tetracycline on RHB750 (C_0 = 50 mg/L; T = 298 K; pH = 3; contact time = 8 h; dose = 20 g/L); (a) removal efficiency and adsorption capacity vs time; (b) PFO; (c) PSO; (d) adsorption capacity vs time

[Dai et al., 2020]. Other studies also reported similar results, suggesting that the aromatic structure of biochar and possible π-π interactions contribute to this behavior [Fan et al., 2018; Popoola, 2020]. The rate constant of the PSO model (k_2 = 0.05906 g/mg.min) suggests fast kinetics, related to the availability of active sites and the possible formation of hydrogen bonds or electrostatic interactions, which is consistent with the assumptions of previous studies [Akhtar et al., 2021]. On the other hand, the lowest constant observed for the PFO model (k_1 = 0.0439 min^{-1}) and its lowest fitted (R^2 = 0.9042) confirm that this model, based on physical mechanisms, does not adequately describe the equilibrium stage.

This behavior has also been described in previous studies [Wang et al., 2017], which highlighted that the larger surface area of activated biochars favors rapid adsorption processes at high temperatures. Compared to other studies with long equilibrium times, which report stabilization after 6 to 10 h [Andrade et al., 2020; Wang et al., 2017], the system evaluated in this study shows high efficiency in a shorter time. This difference can be attributed both to the high accessibility of the active sites of RHB750 and to the presence of specific adsorption mechanisms that allow rapid uptake of TC from the aqueous solution. The PSO model adequately describes not only the initial stage of adsorption but also the equilibrium phase, which is consistent with the observed experimental trend (Figure 4d), where the values of the adsorption capacity over time (q_t) rapidly approach those of the equilibrium adsorption capacity (q_e). Furthermore, the proximity between the experimental adsorption capacity (q_{exp} = 2.50 mg/g) and the adsorption capacity calculated under PSO (q_{calc} = 2.5130 mg/g) supports the validity of the model for this system. These results are consistent with previous studies that indicate that in chemisorption-dominated systems, good agreement between the experimental data and those predicted by the PSO model is achieved [Chen et al., 2016; Zeng et al., 2018].

Finally, it should be noted that although the measured adsorption capacity is relatively low

Table 6. Kinetic parameters for adsorption of tetracycline on HRB750

Kinetic models	Kinetic parameter	Value of parameter
Experimental	q_{exp} (mg/g)	2.5000
Pseudo-first-order	q_{calc} (mg/g)	2.4444
	k_1 (min^{-1})	0.0439
	R^2	0.9042
Pseudo-second-order	q_{calc} (mg/g)	2.5130
	k_2 (g/mg.min)	0.05906
	R^2	0.9988

Note: C_0 = 50 mg/L; T = 298 K; pH = 3; contact time = 8 h; dose = 20 g/L.

compared to other adsorbents, the overall system efficiency is high, highlighting the suitability of RHB750 for the antibiotic-contaminated water treatment process. This is particularly significant given the low cost and wide availability of rice husks as a raw material, making the process both accessible and sustainable.

Adsorption isotherm study

The fitting plots and obtained parameters, presented in Figures 5a–b and Table 7.

The Langmuir model provided a better fit to the experimental data, exhibiting a correlation coefficient R^2 of 0.9843, higher than that of the Freundlich model (R^2 = 0.8578), indicating preferential monolayer adsorption on a homogeneous surface. This behavior was observed in a previous study, which suggested that biochar produced at high temperatures develops a structure with equivalent energy sites, which favors the formation of a uniform adsorbate layer [Wang et al., 2023]. Likewise, the obtained R_L value (0.0065) is in the range of $0 < R_L < 1$, indicating a favorable process from a thermodynamic point of view. The maximum adsorption capacity value (Q_{max}) was 6.009 mg/g, lower than that reported in a previous study, which reported an adsorption capacity of 34.6 mg/g for a biochar produced at 700 °C [Fan et al., 2018]. This can be attributed to differences in the type of precursor and the specific surface area of the material. However, this value is much higher than those reported in the literature for similar materials, confirming the suitability of RHB as an efficient and cost-effective TC adsorbent [Andrade et al., 2020; Chen et al., 2016]. Although the maximum adsorption capacity achieved (6.009 mg/g) can be considered moderate, it was achieved with a dose of 20 g/L, allowing high removal efficiency (97.83%) under practical conditions. This feature is advantageous in real-world applications where the effective treatment of contaminants in high concentrations takes precedence over optimizing the specific capacity.

The presence of high affinity between the active sites of RHB750 and TC is also reflected in the value of the K_L parameter (3.069 L/mg), indicating a strong solute-sorbent interaction. The Freundlich model, for its part, showed a 1/n value of 0.6079, supporting the heterogeneity of the adsorbent surface, although its fit was statistically lower. This is consistent with observations in studies reporting the lack of cooperation between molecules in the adsorption of antibiotics in biochar, strengthening the hypothesis of a mechanism dominated by individual binding to specific active sites [Akhtar et al., 2021]. Complementary studies also demonstrate the applicability of the Langmuir model for systems with high surface affinity materials, as high TC removal (90%) is observed at R_L values within favorable ranges, supporting the general nature of this model in well-designed systems [Al-Kindi and Alnasrawy, 2022].

The results of isothermal analysis show that the Langmuir model best fits the experimental data, indicating monolayer adsorption on a homogeneous surface. The use of biochar from agroindustrial wastes, such as rice husks, is presented as an efficient, accessible, and cost-effective alternative for environmental remediation.

Optimum condition and validation of model

The optimization of the TC adsorption process was performed using the Taguchi L9 experimental design under optimal conditions determined by signal-to-noise ratio (S/N) analysis. Table 8 shows the optimized conditions, including a carbonization temperature of 750 °C, an adsorbent dose of 20 g/L, and a contact time of 4 h, as well

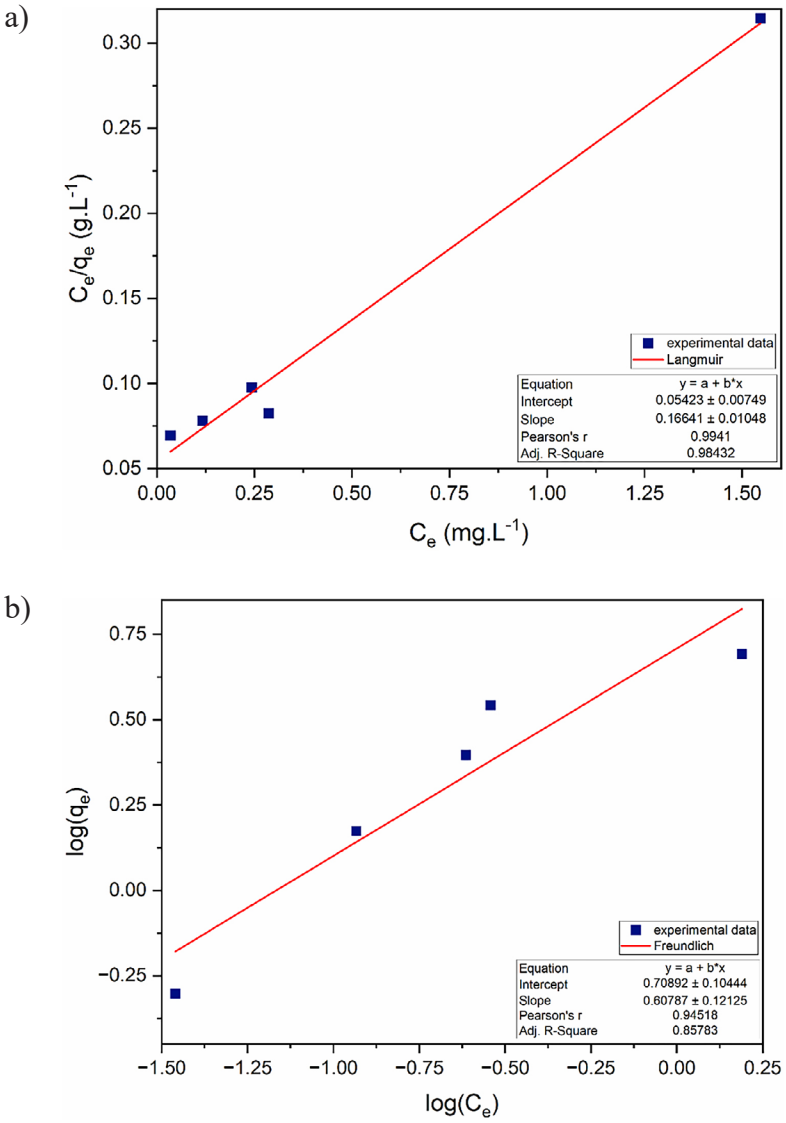

Figure 5. Isotherm models for adsorption of tetracycline on RHB750 (initial concentration = 50 mg/L; temperature = 298 K; pH = 3; contact time = 8 h; dose = 20 g/L); (a) Langmuir; (b) Freundlich

as the efficiency achieved experimentally and the optimal value predicted by the model.

With this configuration, a maximum removal efficiency of 99.51±0.02% was achieved in the experimental tests, which represents a significant improvement over the value of 97.83% achieved in previous tests at the same temperature and dose, but with a contact time of only 1 h. This increase demonstrates that the contact time parameter, although statistically less influential in the ANOVA analysis, plays a relevant role in determining the optimal conditions to achieve a removal close to 100%. The observed performance is consistent with previous results in the literature, which showed that a simultaneous increase in carbonization temperature and adsorbent dose significantly improves the efficiency of TC removal, although with a parallel decrease in specific capacity [S. Wang et al., 2023]. Similarly, other authors have pointed out that at high doses, efficiency can increase to a certain threshold before stabilizing due to effects such as particle agglomeration or saturation of active sites on the surface [Al-Kindi and Alnasrawy, 2022].

The dose of 20 g/L used in this optimization is relatively high compared to other studies that used lower doses. However, its application in this case is justified by the use of rice husk biochar, a readily available and inexpensive agricultural residue that allows its implementation without imposing a significant economic burden. Although the dose of 20 g/L used in this study can be considered high, its economic viability is justified by the low cost and availability of biochar

Table 7. Isotherm parameters of tetracycline adsorption by HRB750

Isotherm models	Isotherm parameter	Value of parameter
Langmuir	Q_{max} (mg/g)	6.009
	K_L (L/mg)	3.069
	R_L	0.006475
	R^2	0.9843
Freundlich	n (L/g)	1.645
	1/n (g/L)	0.6079
	K_f (mg/g)/(mg/L)^n	5.116
	R^2	0.8578

Note: C_0 = 50 mg/L; T = 298 K; pH = 3; contact time = 4 h; dosage = 20 g/L.

Table 8. Optimum condition for maximising the removal efficiency using Taguchi L9

Factors	Optimum conditions	Experimental efficiency, %	Optimal efficiency, %
RHB dose, g/L	20	99.51 ± 0.02	105.78
Carbonization temperature, °C	750		
Contact time	4		

Note: Initial TC concentration = 50 mg/L; final TC concentration = 0.24 ± 0.02.

from agricultural waste such as rice husks. Previous studies reported the successful application of citrus waste biochar for TC adsorption in real wastewater, using even higher doses (70 g/L), with an estimated treatment cost of USD 12.6/m³ [Rizkallah et al., 2023]. In comparison, commercial activated carbon treatment carbon can cost between USD 9.1 and 914.2/m³ due to the higher unit price. This background supports the technical and economic feasibility of using high-dose biochar in real-world water treatment contexts.

Biochar regeneration was not addressed in this study. The literature reports results on the efficiency of biochar desorption and reuse of lignocellulosic waste, depending on the type of contaminant, the regeneration method, and the operating conditions [Dai et al., 2020; Rizkallah et al., 2023]. The feasibility of using rice husk biochar in wastewater treatment has been particularly supported by its ability to adsorb and remove trace contaminants even after reuse [Wang et al., 2023]. Given the low cost and availability of this feedstock, its application as a single-cycle adsorbent may be feasible in certain contexts. However, to further enhance the sustainability of the process, it is suggested to evaluate the performance of biochars in multiple adsorption-desorption cycles. Additionally, rice husk is a low-cost material with a lignocellulose-rich composition and porous structure, which allows for high adsorption efficiency without compromising the sustainability of the process.

Notably, carbonization was carried out with a residence time of one hour, while other studies reported the need for a 2 h heat treatment to achieve similar efficiencies, thus saving energy and operating time [Wang et al., 2023; Zeng et al., 2018]. Comparing the observed experimental efficiency (99.51%) with the optimal efficiency predicted by the model (105.78%), a significant discrepancy is observed, exceeding the realistic physical limit of 100% removal. This excess is due to the limitations of the mathematical model and the software used, which sometimes extrapolate optimal values without considering the inherent constraints of the physical system. Such an overestimation underscores the need to interpret the prediction results within the context of real experimental conditions, taking into account that the model represents an idealized system, while the measured efficiency corresponds to the actual and validated behavior of the process.

Additional validation was performed in artificially contaminated tap water with pure tetracycline and in tap water mixed with the actual contents of medicinal capsules. In both cases, complete contaminant removal (100%) was achieved after 4 h, confirming the robustness of the adsorption system under optimal conditions. It is important to note that the performance in tap water was even better than that in synthetic

solutions, which could be related to the presence of salts and dissolved minerals in the aqueous medium. This hypothesis is supported by a study in which an increase in TC removal was observed from 90% to 95% in real matrices compared to synthetic matrices. This is attributed to the salinization effects induced by dissolved solids, which modify the solute-sorbent interaction [Rizkallah et al., 2023]. In this context, it is concluded that certain ions present in real water can facilitate the formation of electrostatic bonds, improving the overall efficiency of the process. However, the specific impact of coexisting substances such as metal ions or humates was not evaluated in this study. Future work should focus on systematically assessing their influence under realistic wastewater conditions to better understand the applicability of the proposed system. These findings support the high efficiency of the optimized adsorption system for TC removal, which achieves removal rates of over 99% in both synthetic solutions and real matrices.

CONCLUSIONS

This study investigated the efficiency of rice husk biochar in the adsorption of tetracycline. A Taguchi L9 signal-to-noise experimental design was used under the 'Larger is better' condition, considering carbonization temperature, contact time, and adsorbent dosage as key variables. The results showed that under optimal conditions (750 °C, 4 h and 20 g/L), a maximum removal efficiency of 99.51% could be achieved, significantly exceeding the values obtained under non-optimized conditions. Previously, the influence of carbonization temperature on biochar yield was analyzed, observing an inverse correlation between both factors. However, thermal elevation favored the improvement of structural properties, such as surface area (BET), which are essential for the adsorption of organic contaminants. Kinetic analyzes showed better agreement with the pseudo-second-order model, suggesting adsorption dominated by chemical interactions, while equilibrium data were adequately fitted to the Langmuir model, indicating monolayer adsorption on homogeneous surfaces with favorable affinity, in agreement with the obtained R_L values. The efficiency of the system was also validated under real-world conditions with tap water, where an increased removal rate was observed due to the presence of dissolved solids. Taken together, these findings confirm that biochar from agro-industrial wastes, such as rice husks, represents an effective, economical, and environmentally sustainable alternative for the remediation of antibiotic-contaminated water bodies.

Acknowledgements

The authors would like to thank the CIMAYDS research group for its valuable technical support in the development of this study. We also thank the Research Laboratory of the "Facultad de Ingeniería Química e Industrias Alimentarias de la Universidad Nacional Pedro Ruiz Gallo" for providing the equipment and instruments necessary for the comprehensive conduct of this research.

This study was carried out with the support of equipment acquired thanks to the funding granted by Resolution N° 742-2023-R to the "Universidad Nacional Pedro Ruiz Gallo", which allowed the proper development of the experimental activities envisaged in the project.

REFERENCES

1. Akhtar, L., Ahmad, M., Iqbal, S., Abdelhafez, A. A., Mehran, M. T. (2021). Biochars' adsorption performance towards moxifloxacin and ofloxacin in aqueous solution: Role of pyrolysis temperature and biomass type. *Environmental Technology & Innovation, 24*, 101912. https://doi.org/10.1016/j.eti.2021.101912
2. Alghyamah, A. A., Yagoub Elnour, A., Shaikh, H., Haider, S., Manjaly Poulose, A., Al-Zahrani, S. M., Almasry, W. A., Young Park, S. (2021). Biochar/polypropylene composites: A study on the effect of pyrolysis temperature on crystallization kinetics, crystalline structure, and thermal stability. *Journal of King Saud University - Science, 33*(4), 101409. https://doi.org/10.1016/j.jksus.2021.101409
3. Al-Kindi, G. Y., Alnasrawy, S. T. (2022). Tetracycline remove from synthetic wastewater by using several methods. *Journal of Ecological Engineering, 23*(5), 137–148. https://doi.org/10.12911/22998993/146999
4. Andrade, C. A., Zambrano-Intriago, L. A., Oliveira, N. S., Vieira, J. S., Quiroz-Fernández, L. S., Rodríguez-Díaz, J. M. (2020). Adsorption behavior and mechanism of oxytetracycline on rice husk ash: kinetics, equilibrium, and thermodynamics of the process. *Water, Air, & Soil Pollution, 231*(3), 103. https://doi.org/10.1007/s11270-020-04473-6

5. Ari, H. A., Aliyu, A. O., Alani, O. A., Ugya, A. Y., Iduseri, E. O., Runde, M., Abdullahi, M. M. (2024). Enhanced tetracycline degradation using UV/Fenton/titanium dioxide (TiO_2) hybrid process. *Desalination and Water Treatment, 320*, 100819. https://doi.org/10.1016/j.dwt.2024.100819
6. Asadi, H., Ghorbani, M., Rezaei-Rashti, M., Abrishamkesh, S., Amirahmadi, E., Chengrong, C., Gorji, M. (2021). Application of rice husk biochar for achieving sustainable agriculture and environment. *Rice Science, 28*(4), 325–343. https://doi.org/10.1016/j.rsci.2021.05.004
7. Atta, H. A., Hummadi, K. K., M-Ridha, M. J. (2022). The application of response surface methodology and Design-Expert® for analysis of ciprofloxacin removal from aqueous solution using raw rice husk: Kinetic and isotherm studies. *Desalination and Water Treatment, 248*, 203–216. https://doi.org/10.5004/dwt.2022.28074
8. Aziz, S., Uzair, B., Ali, M. I., Anbreen, S., Umber, F., Khalid, M., Aljabali, A. AA., Mishra, Y., Mishra, V., Serrano-Aroca, Á., Naikoo, G. A., El-Tanani, M., Haque, S., Almutary, A. G., Tambuwala, M. M. (2023). Synthesis and characterization of nanobiochar from rice husk biochar for the removal of safranin and malachite green from water. *Environmental Research, 238*, 116909. https://doi.org/10.1016/j.envres.2023.116909
9. Basheer, A. A. (2018). New generation nano-adsorbents for the removal of emerging contaminants in water. *Journal of Molecular Liquids, 261*, 583–593. https://doi.org/10.1016/j.molliq.2018.04.021
10. Bushra, B., Remya, N. (2024). Biochar from pyrolysis of rice husk biomass—Characteristics, modification and environmental application. *Biomass Conversion and Biorefinery, 14*(5), 5759–5770. https://doi.org/10.1007/s13399-020-01092-3
11. Campos, P., Miller, A. Z., Knicker, H., Costa-Pereira, M. F., Merino, A., De la Rosa, J. M. (2020). Chemical, physical and morphological properties of biochars produced from agricultural residues: Implications for their use as soil amendment. *Waste Management, 105*, 256–267. https://doi.org/10.1016/j.wasman.2020.02.013
12. Chen, Y., Wang, F., Duan, L., Yang, H., Gao, J. (2016). Tetracycline adsorption onto rice husk ash, an agricultural waste: Its kinetic and thermodynamic studies. *Journal of Molecular Liquids, 222*, 487–494. https://doi.org/10.1016/j.molliq.2016.07.090
13. Dai, J., Meng, X., Zhang, Y., Huang, Y. (2020). Effects of modification and magnetization of rice straw derived biochar on adsorption of tetracycline from water. *Bioresource Technology, 311*. Scopus. https://doi.org/10.1016/j.biortech.2020.123455
14. Dou, Z., Li, C., Ji, X., Lai, J., Fu, Q., Liu, H., Gong, S., Wu, J. (2024). Efficient degradation of tetracycline in wastewater by novel biochar-based photocatalytic materials: Performance, photocatalytic mechanism and degradation pathways. *Research on Chemical Intermediates.* https://doi.org/10.1007/s11164-024-05451-x
15. Fan, S., Wang, Y., Li, Y., Wang, Z., Xie, Z., Tang, J. (2018). Removal of tetracycline from aqueous solution by biochar derived from rice straw. *Environmental Science and Pollution Research International, 25*(29), 29529–29540. https://doi.org/10.1007/s11356-018-2976-0
16. Gan, C., Zhou, Q., Sheng, M., Hu, Z., Li, Y., Zhou, J., Bian, F., Sun, B., Jiang, H. (2024). Microwave-mediated ultrafast solid-state construction of O vacancies enriched cobalt oxide/nitrogen carbon aerogel toward efficient tetracycline degradation with peroxymonosulfate. *Journal of Cleaner Production, 434*, 140417. https://doi.org/10.1016/j.jclepro.2023.140417
17. Han, Q. F., Zhao, S., Zhang, X. R., Wang, X. L., Song, C., Wang, S. G. (2020). Distribution, combined pollution and risk assessment of antibiotics in typical marine aquaculture farms surrounding the Yellow Sea, North China. *Environment International, 138*, 105551. https://doi.org/10.1016/j.envint.2020.105551
18. Harguindeguy, M., Pochat-Bohatier, C., Sanchez-Marcano, J., Belleville, M.-P. (2024). Enzymatic degradation of tetracycline by Trametes versicolor laccase in a fluidized bed reactor. *Science of The Total Environment, 907*, 168152. https://doi.org/10.1016/j.scitotenv.2023.168152
19. Jang, H. M., Yoo, S., Choi, Y.-K., Park, S., Kan, E. (2018). Adsorption isotherm, kinetic modeling and mechanism of tetracycline on Pinus taeda-derived activated biochar. *Bioresource Technology, 259*, 24–31. https://doi.org/10.1016/j.biortech.2018.03.013
20. Jeganathan, Y., Asharp, T., Nadarajah, K. (2024). Adsorptive behavior of engineered biochar /hydrochar for tetracycline removal from synthetic wastewater. *Environmental Pollution, 345*. https://doi.org/10.1016/j.envpol.2024.123452
21. Jia, Y., Shi, S., Liu, J., Su, S., Liang, Q., Zeng, X., Li, T. (2018). Study of the effect of pyrolysis temperature on the cd2+ adsorption characteristics of biochar. *Applied Sciences, 8*(7), Article 7. https://doi.org/10.3390/app8071019
22. Jiang, T.-J., Morgan, H. M., Tsai, W.-T., Chien, H., Yen, T.-B., Lee, Y.-R. (2024). Thermochemical conversion of biomass into biochar: enhancing adsorption kinetics and pore properties for environmental sustainability. *Sustainability, 16*(15), Article 15. https://doi.org/10.3390/su16156623
23. Jindo, K., Mizumoto, H., Sawada, Y., Sanchez-Monedero, M. A., Sonoki, T. (2014). Physical and chemical characterization of biochars derived

from different agricultural residues. *Biogeosciences, 11*(23), 6613–6621. https://doi.org/10.5194/bg-11-6613-2014

24. Liu, Z., Jia, M., Li, Q., Lu, S., Zhou, D., Feng, L., Hou, Z., Yu, J. (2023). Comparative analysis of the properties of biochars produced from different pecan feedstocks and pyrolysis temperatures. *Industrial Crops and Products, 197*, 116638. https://doi.org/10.1016/j.indcrop.2023.116638
25. Nwajiaku, I. M., Olanrewaju, J. S., Sato, K., Tokunari, T., Kitano, S., Masunaga, T. (2018). Change in nutrient composition of biochar from rice husk and sugarcane bagasse at varying pyrolytic temperatures. *International Journal of Recycling of Organic Waste in Agriculture, 7*(4), 269–276. https://doi.org/10.1007/s40093-018-0213-y
26. Oberoi, A. S., Jia, Y., Zhang, H., Khanal, S. K., Lu, H. (2019). Insights into the fate and removal of antibiotics in engineered biological treatment systems: a critical review. *Environmental Science & Technology, 53*(13), 7234–7264. https://doi.org/10.1021/acs.est.9b01131
27. Phakathi, N. A., Tichapondwa, S. M., Chirwa, E. M. N. (2022). Photocatalytic degradation of tetracycline using visible-light-driven porous g- C3N4 nanosheets catalyst. *Chemical Engineering Transactions, 96*, 391–396. https://doi.org/10.3303/CET2296066
28. Popoola, L. T. (2020). Tetracycline and sulfamethoxazole adsorption onto nanomagnetic walnut shell-rice husk: Isotherm, kinetic, mechanistic and thermodynamic studies. *International Journal of Environmental Analytical Chemistry, 100*(9), 1021–1043. https://doi.org/10.1080/03067319.2019.1646739
29. Rizkallah, B. M., Galal, M. M., Matta, M. E. (2023). Characteristics of tetracycline adsorption on commercial biochar from synthetic and real wastewater in batch and continuous operations: Study of removal mechanisms, isotherms, kinetics, thermodynamics, and desorption. *Sustainability, 15*(10), Article 10. https://doi.org/10.3390/su15108249
30. Rodríguez, F., Montoya-Ruiz, C., Estiati, I., Saldarriaga, J. F. (2020). Removal of drugs in polluted waters with char obtained by pyrolysis of hair waste from the tannery process. *ACS Omega, 5*(38), 24389–24402. https://doi.org/10.1021/acsomega.0c02768
31. Saghir, S., Pu, C., Fu, E., Wang, Y., Xiao, Z. (2022). Synthesis of high surface area porous biochar obtained from pistachio shells for the efficient adsorption of organic dyes from polluted water. *Surfaces and Interfaces, 34*, 102357. https://doi.org/10.1016/j.surfin.2022.102357
32. Sukarta, I. N., Suyasa, I. W. B., Mahardika, I. G., Suprihatin, I. E., Sastrawidana, I. D. K. (2025). Innovation of Remazol yellow FG dye adsorption using biochar from coffee fruit shell waste. *Journal of Ecological Engineering, 26*(1), 273–285. https://doi.org/10.12911/22998993/195754
33. Sun, J., He, F., Pan, Y., Zhang, Z. (2017). Effects of pyrolysis temperature and residence time on physicochemical properties of different biochar types. *Acta Agriculturae Scandinavica, Section B — Soil & Plant Science, 67*(1), 12-22. https://doi.org/10.1080/09064710.2016.1214745
34. Sun, Z., Wei, Q., Hua, W., Chen, M., Yuan, Q., Yi, B., Ok, Y. S. (2024). Engineered biochar for advanced oxidation process towards tetracycline degradation: Role of iron and graphitic structure. *Journal of Environmental Chemical Engineering, 12*(6), 114290. https://doi.org/10.1016/j.jece.2024.114290
35. Thairattananon, P., Le, G. T. T., Matsumura, Y., Wu, K. C. W., Charinpanitkul, T. (2024). Effect of pyrolysis temperature on characteristics of tunable magnetic biochar synthesized from watermelon rind and its tetracycline adsorption performance. *Journal of the Taiwan Institute of Chemical Engineers, 160*, 105345. https://doi.org/10.1016/j.jtice.2024.105345
36. Tsai, W.-T., Lin, Y.-Q., Huang, H.-J. (2021). Valorization of rice husk for the production of porous biochar materials. *Fermentation, 7*(2), Article 2. https://doi.org/10.3390/fermentation7020070
37. Vilca, F. Z., Galarza, N. C., Tejedo, J. R., Cuba, W. A. Z., Quiróz, C. N. C., Tornisielo, V. L. (2021). Occurrence of residues of veterinary antibiotics in water, sediment and trout tissue (*Oncorhynchus mykiss*) in the southern area of Lake Titicaca, Peru. *Journal of Great Lakes Research, 47*(4), 1219–1227. https://doi.org/10.1016/j.jglr.2021.04.012
38. Wang, B., Wang, T., Su, H. (2022). Hydrodynamic cavitation (HC) degradation of tetracycline hydrochloride (TC). *Separation and Purification Technology, 282*, 120095. https://doi.org/10.1016/j.seppur.2021.120095
39. Wang, H., Chu, Y., Fang, C., Huang, F., Song, Y., Xue, X. (2017). Sorption of tetracycline on biochar derived from rice straw under different temperatures. *PLoS ONE, 12*(8). https://doi.org/10.1371/journal.pone.0182776
40. Wang, J., Chen, X., Sun, H., Li, X., Lu, Q., Qin, P., Yang, Y., Lai, D., Luo, L., Peng, X., Yang, Y., Wu, Z. (2025). Accelerated removal and mechanism of tetracycline from water using immobilized bacteria combined with microalgae. *Journal of Environmental Chemical Engineering, 13*(2), 115424. https://doi.org/10.1016/j.jece.2025.115424
41. Wang, S., Chen, Y., Ge, S., Liu, Z., Meng, J. (2023). Adsorption characterization of tetracycline antibiotics on alkali-functionalized rice husk biochar and its evaluation on phytotoxicity to seed germination. *Environmental Science and Pollution Research, 30*(58), 122420–122436. https://doi.org/10.1007/s11356-023-30900-2.

42. Yu, Z., Zhang, C., Zheng, Z., Hu, L., Li, X., Yang, Z., Ma, C., Zeng, G. (2017). Enhancing phosphate adsorption capacity of SDS-based magnetite by surface modification of citric acid. *Applied Surface Science, 403*, 413–425. https://doi.org/10.1016/j.apsusc.2017.01.163
43. Zeng, Z., Tian, S., Liu, Y., Tan, X., Zeng, G., Jiang, L., Yin, Z., Liu, N., Liu, S., Li, J. (2018). Comparative study of rice husk biochars for aqueous antibiotics removal. *Journal of Chemical Technology & Biotechnology, 93*(4), 1075–1084. https://doi.org/10.1002/jctb.5464
44. Zhang, F., Wang, J., Tian, Y., Liu, C., Zhang, S., Cao, L., Zhou, Y., Zhang, S. (2023). Effective removal of tetracycline antibiotics from water by magnetic functionalized biochar derived from rice waste. *Environmental Pollution, 330*, 121681. https://doi.org/10.1016/j.envpol.2023.121681
45. Zhang, H., Chen, C., Gray, E. M., Boyd, S. E. (2017). Effect of feedstock and pyrolysis temperature on properties of biochar governing end use efficacy. *Biomass and Bioenergy, 105*, 136–146. https://doi.org/10.1016/j.biombioe.2017.06.024
46. Zhang, X., Hou, J., Zhang, S., Cai, T., Liu, S., Hu, W., Zhang, Q. (2024). Standardization and micromechanistic study of tetracycline adsorption by biochar. *Biochar, 6*(1), 12. https://doi.org/10.1007/s42773-023-00299-7
47. Zhang, X., Zhang, P., Yuan, X., Li, Y., Han, L. (2020). Effect of pyrolysis temperature and correlation analysis on the yield and physicochemical properties of crop residue biochar. *Bioresource Technology, 296*, 122318. https://doi.org/10.1016/j.biortech.2019.122318
48. Zhang, Y., Liu, F., Zhong, L., Dong, Z., Chen, C., Xu, Z. (2023). Reusable and environmentally friendly cellulose nanofiber/titanium dioxide/chitosan aerogel photocatalyst for efficient degradation of tetracycline. *Applied Surface Science, 641*, 158425. https://doi.org/10.1016/j.apsusc.2023.158425
49. Zhao, H., Li, J., Li, S., Jiang, Y., Du, L. (2024). Evaluation and optimization of six adsorbents for removal of tetracycline from swine wastewater: Experiments and response surface analysis. *Journal of Environmental Management, 368*, 122170. https://doi.org/10.1016/j.jenvman.2024.122170