



Mg-impregnated rice husk biochar in fixed-bed columns: high-capacity continuous-flow removal of nitrate and phosphate from wastewater

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Abstract

Wastewater contaminated with nitrate and phosphate requires effective removal to prevent eutrophication in water bodies, a process that can lead to significant environmental and economic issues. Magnesium-modified rice husk biochar was prepared, characterized, and used for the removal of nitrate and phosphate from both synthetic and real wastewater through fixed-bed adsorption. The influence of operational variables such as flow rate (5.5–20 mL/min), bed height (4–8 cm), and initial influent concentration (20–100 mg/L) on breakthrough curves was investigated. The results revealed that as flow rate and initial concentration increased, the breakthrough curves became steeper, while their slopes decreased as bed height increased. Adsorption capacities of 9.4 mg/g and 78 mg/g were found for nitrate and phosphate, respectively, for synthetic water. Additionally, the competitive removal of nitrate and phosphate from real wastewater was studied, finding adsorption capacities of 1.4 mg/g for nitrate and 2.4 mg/g for phosphate, with a flow rate of 5.5 mL/min, bed heights ranging from 4 to 8 cm, natural pH (6.2), ambient temperature (20 °C), and respective nitrate and phosphate concentrations of 14.9 mg/L and 3.3 mg/L, being the main finding of this research the application of the studied biochar to real wastewater based on the prior study of the operational variables of the adsorption process in fixed-bed columns. Overall, Thomas, Bohart-Adams, Yoon-Nelson, and Clark models provided good fits for the breakthrough curves, enabling their application for the design and implementation of alternative treatments in wastewater treatment plants.

Keywords Rice husk biochar · Chemical modification with Mg · Fixed bed adsorption · Phosphate · Nitrate

1 Introduction

Municipal and industrial wastewater can contain excessive concentrations of nitrate and phosphate, which can promote the eutrophication of water bodies. Regulations controlling the discharge of effluents from wastewater treatment plants are becoming increasingly stringent in various countries, reducing the discharge limits of treated water into receiving water bodies [1]. These nutrients accelerate the growth of aquatic plants, which, upon dying, are decomposed by aquatic microorganisms, decreasing the oxygen available for aerobic aquatic life, leading to economic and ecosystem losses [2].

For this reason, it is necessary to implement efficient treatment technologies to remove nutrients from water, particularly phosphate, which have to be reduced to very low concentrations in the treated effluent. It is considered that phosphate levels of 0.1 mg/L can promote

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eutrophication in water bodies, as phosphate is the limiting substance for the growth of phytoplankton and aquatic plants [3]. Additionally, elevated concentrations of nitrate and phosphate cause other health issues in drinking water, such as: infantile cyanosis syndrome (blue baby syndrome), hepatic damage, respiratory tract diseases, cancer, osteoporosis, urine damage, among others [4].

These nutrients have been removed using various technologies, such as membrane processes, including electrodialysis and reverse osmosis; chemical precipitation; biological oxidation, such as the bioremediation process with microalgae-bacteria, among others [5–7]. However, these are considered to have high operational costs compared to adsorption using agro-industrial waste, which is considered a low-cost process and requires environmental management to minimize its negative environmental impacts when not used sustainably. An example of this is rice husk, a byproduct of rice cultivation, which generates approximately 106 million tons out of the 530 million tons produced annually by rice farming [8]. Rice cultivation is one of the major contributors to global methane emissions (30%) and nitrous oxide emissions (11%) [9]. Therefore, it is crucial to mitigate the negative environmental impacts associated with rice cultivation and its byproducts from an environmental management perspective.

Biochar, as a product obtained from the pyrolysis of various biomass sources, including rice husk, has gained significant interest as an adsorbent due to its high adsorption capacities in water decontamination and its potential use as a soil amendment, enhancing carbon dioxide and other greenhouse gases capture, thus contributing positively to the environment [10]. Previous studies have shown the removal of nitrate and phosphate using unmodified rice husk biochar. For example, Konneh et al. [11] found nitrate removal efficiencies between 35 and 65% (0.13 to 13 mg/L) with adsorbent doses ranging from 0.8 to 8 g/L for initial nitrate concentrations between 13 and 130 mg/L. Fatima et al. [12] reported nitrate and phosphate removal efficiencies in batch mode between 40 and 95% (47 to 95 mg/g) for initial concentrations of 50 mg/L of nitrate and 100 mg/L of phosphate, applying an adsorbent dose of 1 g/L.

In a previous study conducted by the authors [13], the adsorption efficiency of nitrate and phosphate was evaluated using various bioadsorbents, including untreated rice husk and corn stalk, as well as their respective biochars without chemical modification. The results showed that while the untreated materials outperformed the biochars, they were ineffective for phosphate removal. Moreover,

the biochars failed to remove either nitrate or phosphate from synthetic water in batch mode, differing from the studies cited before.

To address this limitation, rice husk biochar was modified with magnesium chloride, as Mg is environmentally friendly and abundant in the biosphere [14]. This chemical modification significantly enhanced the removal of both nitrate and phosphate from synthetic waters, in both individual and competitive adsorption scenarios.

Building on this previous work, the present study shifts the focus to a fixed-bed column system, as most adsorption studies on nitrate and phosphate using magnesium-impregnated rice husk biochar have been limited to batch mode and synthetic water. The authors have not found studies examining the operational variables of magnesium-impregnated rice husk biochar in fixed-bed columns, particularly the effects of initial influent concentration, bed depth, and flow rate on adsorption capacity and nitrate and phosphate removal efficiency.

The adsorption of nutrients in fixed-bed columns using rice husk biochar presents clear environmental and economic advantages compared with other adsorbents. Environmentally, pyrolysis generates fewer greenhouse gases and requires less energy, while biochar exhibits high nutrient removal capacity relative to commercial adsorbents such as activated carbon or other biomass-derived materials [15, 16]. Furthermore, biochar can be reused as a soil amendment, providing additional benefits including greenhouse gas mitigation, water conservation, and reduced fertilizer requirements [4, 11, 16, 17]. Most of these studies, however, were conducted in batch mode; studying breakthrough curves in fixed-bed columns allows better prediction of effluent quality and compliance with wastewater discharge regulations, offering a novel contribution of this work [18, 19]. From an economic perspective, rice husk biochar is advantageous due to the abundance of rice husk [4], which lowers production costs, combined with simple preparation compared to chemically activated or modified adsorbents [20]. Its versatility is further highlighted by its effectiveness across a range of pH conditions (acidic, neutral, and basic) [4, 21], and by additional savings in water and fertilizer when used as a soil amendment.

Therefore, the objectives of this research were: (1) to study the operational variables for the adsorption of nitrate and phosphate in aqueous solution using magnesium-modified rice husk biochar in continuous mode (2) to mathematically model the dynamic adsorption process, and (3) to determine the removal efficiency of nitrate and phosphate from a real wastewater, in order to assess its applicability at an industrial scale as a sustainable alternative for wastewater decontamination.

2 Materials and methods

2.1 Materials

The rice husk was purchased from a distributor in Navarra, Spain. The following reagents were used, all of which were of analytical grade: standard solutions of 1000 mg/L nitrate and phosphate (both 99% purity, CPA Chem, Bulgaria), NaNO_3 (99% purity, Panreac AppliChem, Spain), KH_2PO_4 (99% purity, Panreac AppliChem, Spain), MgCl_2 (99% purity, Sigma-Aldrich, Germany), ascorbic acid (99% purity, Panreac AppliChem, Spain), ammonium molybdate tetrahydrate (99% purity, Panreac AppliChem, Spain), and potassium antimonyl tartrate trihydrate (99% purity, Sigma-Aldrich, Germany). All solutions were prepared using tap water.

2.2 Adsorbent preparation

The magnesium-modified rice husk biochar (RHB-Mg) was prepared based on adaptations of the methodologies proposed by Tran et al. [21] and Zhang et al. [22]. Sixty grams of rice husk were washed with approximately 1 L of distilled water, then dried at 105 °C for 24 h. The impregnation was carried out at room temperature for 2 h with stirring, mixing the dry biomass with a 3.3 M MgCl_2 solution at a biomass (g)/water (mL) ratio of 1/15 using a magnetic stirrer at 400 rpm. Subsequently, the Mg-modified material was dried in an oven at 80 °C for 24 h.

The biochar was then produced using a muffle furnace (Nabertherm GmbH, Germany). The first step involved inerting the pyrolysis zone with a nitrogen flow of 34 L/h for 30 min. The second stage consisted of carbonizing the precursor material at 400 °C for 1 h with a heating rate of 15 °C/min. Finally, RHB-Mg was removed from the pyrolysis zone after reaching ambient temperature and was applied to the adsorption tests in the present study. The biochar prepared in this study differs from that used in the batch studies [13] due to variations in the biomass origin and pyrolysis method. Therefore, it was characterized to account for these differences.

2.3 Adsorbent characterization

The adsorbent was characterized using the following techniques: (1) Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDX) (ZEISS EVO LS 15 with EDX, Germany); (2) Infrared Spectrophotometry (FTIR) (VARIAN FTIR 670, United States); (3) Point of Zero Charge (pH_{PZC}): Determined based on the methods outlined by Şentürk & Yıldız [23] and Nordin et al. [24]; and (4) Surface area determination using

the Brunauer-Emmett-Teller (BET) isotherm with a surface area analyzer (ASAP 2020 Micromeritics, United States). All tests were performed on the precursor material (raw rice husk) and Mg-modified biochar (RHB-Mg) to evaluate the physical and chemical changes of the biochar compared to the starting material. SEM-EDX measurements were carried out before and after the adsorption of nitrate and phosphate to verify the adsorption of these two nutrients. Additionally, the average pore size of RHB-Mg was determined using the BET technique, while the average particle size was estimated through SEM image analysis using ImageJ software [25]. The density was calculated as the mass/volume ratio of the biochar under study.

2.4 Fixed bed adsorption experiments

Experiments were conducted in a fixed-bed column at room temperature (approximately 20 °C) and natural pH (approximately 7), as batch screening experiments revealed that these two variables did not affect the removal efficiency of phosphate and nitrate in aqueous solutions [13].

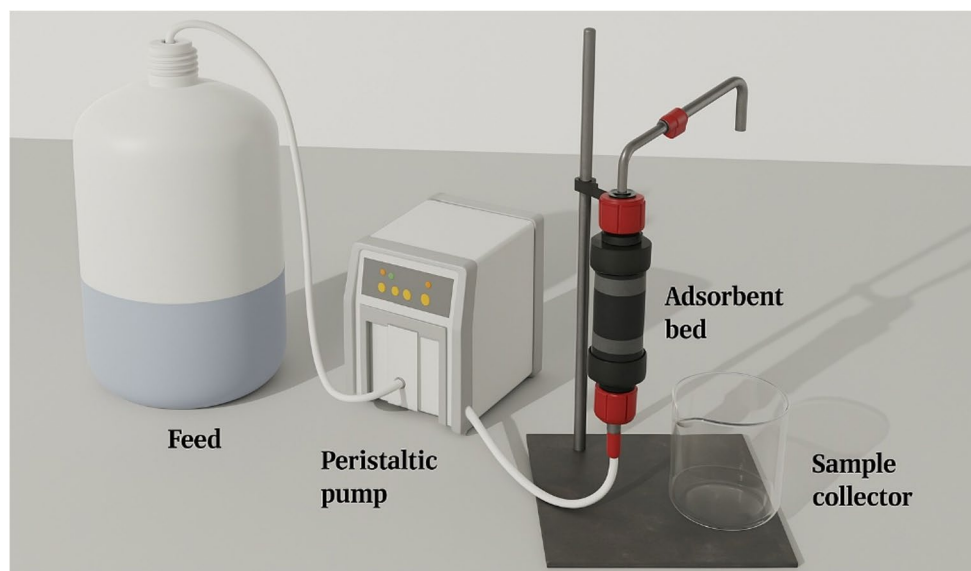
The column used was made of Pyrex glass, with an internal diameter of 1.86 cm and a height of 12.5 cm (see Fig. 1). It was packed with RHB-Mg, and the height was fixed by covering the bed with glass wool at both the top and bottom to prevent displacement of the adsorbent. Most experiments were conducted with a bed height of 4 cm, corresponding to 1.6 g of RHB-Mg, using a peristaltic pump (Heidolph PD5201, Germany) to drive the upward flow. When bed heights of 6 cm and 8 cm were used, the masses of RHB-Mg were 2.4 g and 3.2 g, respectively.

In all experiments, samples were collected, and the remaining concentration of nitrate and phosphate were determined using the methods defined in the Standard Methods for the Examination of Water and Wastewater: Spectroscopy (SM -4500- $\text{NO}_3\text{-B}$) and Spectroscopy (SM 4500-PE), employing the JASCO V-630 spectrophotometer. For this, absorbances were measured at wavelengths of 220 nm and 275 nm for nitrate, and 880 nm for phosphate, determining the concentrations of these two contaminants from calibration curves established on the spectrophotometer used. The methods and references for alkalinity and COD were respectively: Volumetric (SM 2320-B) and closed reflux colorimetric (SM 5220-D).

2.4.1 Effect of flow rate on nitrate and phosphate adsorption

To study the effect of flow rate on the removal efficiency of nitrate and phosphate in individual solutions, two volumetric flow rates were investigated: 5.5 and 20 mL/min, with fixed concentrations of 50 mg/L for nitrate and 100 mg/L

Fig. 1 Setup of continuous flow experiments



for phosphate. The solutions were prepared using NaNO_3 for nitrate and KH_2PO_4 for phosphate, and using tap water which had concentrations of 6.27 ± 0.97 mg/L of nitrate and 0.024 ± 0.002 mg/L of phosphate.

2.4.2 Effect of initial concentration of nitrate and phosphate

In order to evaluate the effect of the initial concentration of nitrate and phosphate, two additional concentrations were analyzed for nitrate and phosphate, at fixed values of the flow rate ($Q = 5.5$ mL/min) and bed height ($Z = 4$ cm). These concentrations were 30 mg/L and 20 mg/L for nitrate, and 50 mg/L and 20 mg/L for phosphate, respectively.

2.4.3 Effect of bed height

The effect of bed height on the removal of nitrate and phosphate was investigated by fixing the flow rate ($Q = 5.5$ mL/min) and the initial concentration at 50 mg/L for nitrate and 100 mg/L for phosphate. Two bed heights were analyzed: 6 cm and 8 cm.

2.4.4 Adsorption study with real wastewater

The application of RHB-Mg as adsorbent was evaluated in the effluent from the biological treatment at the Lagares Wastewater Treatment Plant (WTP Lagares) in the municipality of Vigo, Spain. The wastewater sample had 14.9 mg/L of nitrate, 3.3 mg/L of phosphate, 38.2 mg/L of COD, 30.0 mg/L of alkalinity as CaCO_3 , and a pH of 6.2. The operational variables for the adsorption of the real wastewater were: flow rate ($Q = 5.5$ mL/min), natural pH, ambient temperature, and two bed heights (4 cm and 8 cm).

2.5 Determination of the breakthrough curve parameters

The breakthrough curve parameters were determined to identify operational variables, such as: breakthrough time (t_b), which represents the moment when the effluent concentration reaches 5% of the initial concentration ($C_t/C_0 = 0.05$), and saturation time (t_s), when the effluent concentration reaches 95% of the initial concentration ($C_t/C_0 = 0.95$) [26]. The adsorption capacity of RHB-Mg (q_{bed}), expressed in mg of contaminant removed per gram of RHB-Mg, was calculated using Eq. (1):

$$q_{bed} = \int_{t=0}^{t=t_{oper}} \left(\frac{C_0 - C_t}{m} \right) Q dt \quad (1)$$

Where: $[t_{oper}]$ = operational time of the column in minutes, $[m]$ = mass of the adsorbent used in the column, in g. $[Q]$ = flow rate in L/min, $[q_{bed}]$ = adsorption capacity of RHB-Mg in mg/g, $[C_0]$ and $[C_t]$ represent the initial concentrations (mg/L) of the contaminant and the remaining concentration measured at a specific time in the effluent of the column, respectively.

Equation (1) was solved by finding the area under the breakthrough curve graph: C_t/C_0 vs. time, using the composite trapezoidal numerical integration method as follows (Eq. 2):

$$I = \frac{b-a}{2n} \left[f(x_0) + 2 \sum_{i=1}^{n-1} f(x_i) + f(x_n) \right] \quad (2)$$

Once the area under the curve (I) in minutes was determined, q_{bed} was calculated using Eq. (3):

$$q_{bed} = \frac{1}{1000} \left(\frac{C_0 \cdot Q \cdot I}{m} \right) \quad (3)$$

The mass transfer zone (MTZ) corresponds to the region of the bed where contaminants are adsorbed most rapidly and efficiently, where there is a greater exchange between the adsorbate and adsorbent molecules [27]. MTZ was calculated using Eq. (4):

$$MTZ = Z \left(1 - \frac{t_b}{t_s} \right) \quad (4)$$

Where [Z] is the bed depth in cm, [t_b]= breakthrough time and [t_s]= saturation time, both in min. The effluent volume (V_e) during the operation of the column was estimated using Eq. (5):

$$V_e = Q \cdot t_{oper} \quad (5)$$

Where [t_{oper}]= operational time of the column (min). The removal percentage or efficiency (E%) of nitrate and phosphate was estimated using Eq. (6):

$$E (\%) = \frac{q_{total}}{m_{total}} * 100 \quad (6)$$

Where [m_{total}]: is the amount of adsorbate (nitrate or phosphate) accumulated in the bed, expressed in mg, and was estimated using Eq. (7); [q_{total}]: total mass of contaminant adsorbed is given by Eq. (8):

$$m_{total} = \frac{Q * C_0 * t_{oper}}{1000} \quad (7)$$

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{oper}} (C_0 - C_t) dt \quad (8)$$

Where [C_t]= remaining concentration measured at a specific time in the effluent of the column (mg/L). Equation (8) was solved by using Eq. (2) to find the area under the curve (I) of the C_t/C_0 vs. time graph, yielding Eq. (9):

$$q_{total} = \frac{Q \cdot C_0 \cdot I}{1000} \quad (9)$$

Where: [Q]: flow rate (L/min), [t_{oper}]= operational time of the column (min), [C_0] and [C_t] represent the initial concentrations (mg/L) of the contaminant and the remaining concentration measured at a specific time in the effluent of the column, respectively.

2.6 Fixed bed modelling

The adsorption data from the continuous flow experiments were modeled using four empirical mathematical models: Thomas, Yoon-Nelson, Clark, and Bohart-Adams, in order to: (1) study the breakthrough curves in more detail, and (2) estimate the maximum adsorption capacity and the average breakthrough time of the column adsorption process. These models were estimated using the Solver tool included in Microsoft Excel and the CAVS- Adsorption Evaluation Software.

Thomas model A widely used model for fixed-bed column adsorption studies to predict the performance of column operations and applied to evaluate the adsorption rate constant and the maximum adsorption of the adsorbate [28–30]. The non-linearized Eq. (10) can be expressed as follows:

$$\frac{C_t}{C_0} = \frac{1}{1 + e^{\frac{(k_{Th})(q_0)(x)}{v} - (k_{Th})(C_0)(t)}} \quad (10)$$

Where: [k_{Th}]= Thomas rate constant ($\text{mL min}^{-1} \text{mg}^{-1}$), [q_0]= amount of adsorbate in equilibrium (mg/g), [x]= amount of adsorbent in the column (g), [v]= flow rate of the solution passing through the column (mL min^{-1}), [C_t/C_0]= relationship between the concentrations of the effluent (C_t) and the influent (C_0), both in mg/L and [t] operation time (min).

Yoon-Nelson model It is one of the simplest models used to predict the exhaustion time and the behavior of the adsorption process for a given adsorbate concentration [28, 31, 32]. The model is given by Eq. (11):

$$\frac{C_t}{C_0} = \frac{1}{1 + e^{(k_{YN})(\tau - t)}} \quad (11)$$

Where: [k_{YN}]= Yoon-Nelson rate constant (min^{-1}), [τ] operation time required to reach 50% breakthrough (min). τ and k_{YN} are obtained from the intersection and slope of the graph by applying the Yoon-Nelson equation, respectively, [C_t/C_0]= relationship between the concentrations of the effluent (C_t) and the influent (C_0), both in mg/L and [t] operation time (min).

Clark model It is based on the use of a mass transfer concept combined with the Freundlich adsorption isotherm [33, 34]. Equation (12) represents the non-linearized model:

$$\frac{C_t}{C_0} = \left(\frac{1}{1 + Ae^{-rt}} \right)^{1/(n-1)} \quad (12)$$

Where: $[A]$ (dimensionless) and $[r]$ (min^{-1}) are the parameters of Clark, $[n]$ is the Freundlich parameter (dimensionless), $[C_t/C_0]$ = relationship between the concentrations of the effluent (C_t) and the influent (C_0), both in mg/L and $[t]$ operation time (min).

Bohart-Adams model It is a model primarily used to model the initial part of the breakthrough curve [27]. Equation (13) represents the Bohart-Adams model:

$$\frac{C_t}{C_0} = \frac{1}{1 + e^{\left(\frac{k_{BA} Z N_0}{F} - k_{BA} C_0 t\right)}} \quad (13)$$

Where: $[k_{BA}]$ Bohart-Adams coefficient ($\text{L mg}^{-1} \text{min}^{-1}$), $[N_0]$ adsorbent sorption capacity (mg L^{-1}), $[Z]$ Bed height (cm), $[F]$ superficial velocity (cm min^{-1}), $[C_t/C_0]$ = relationship between the concentrations of the effluent (C_t) and the influent (C_0), both in mg/L and $[t]$ operation time (min).

2.7 Error analysis

The error of the mathematical models used was calculated using Eq. (14) of the Root Mean Square Error (RMSE):

$$RSME = \sqrt{\frac{1}{n} \sum_{i=1}^n (C_{exp} - C_{cal})_i^2} \quad (14)$$

Where: $[n]$ is the number of experimental points, $[C_{exp}]$ and $[C_{cal}]$ correspond to the adsorbate concentration at a given time, determined experimentally and calculated using the model, respectively.

Additionally, the coefficient of determination (R^2) of the adsorption mathematical models was calculated to evaluate the goodness of fit of these models, Eq. (15).

$$R^2 = 1 - \frac{SME}{SST} = 1 - \frac{\sum_{i=1}^n (C_{exp} - C_{cal})_i^2}{\sum_{i=1}^n (C_{exp,i} - \bar{C}_{exp})^2} \quad (15)$$

Where: $[MSE]$ = Mean Squared Error, $[SST]$: Total Sum of Squares, $[C_{exp,i}]$ = Adsorbate concentrations measured over time, $[\bar{C}_{exp}]$ =The average concentration of the adsorbates measured over time.

3 Results and discussion

3.1 Characterization of adsorbents

3.1.1 Fourier-transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR)

Figure 2 shows the FTIR spectrum of RHB-Mg and its comparison with the starting material. The spectrum of

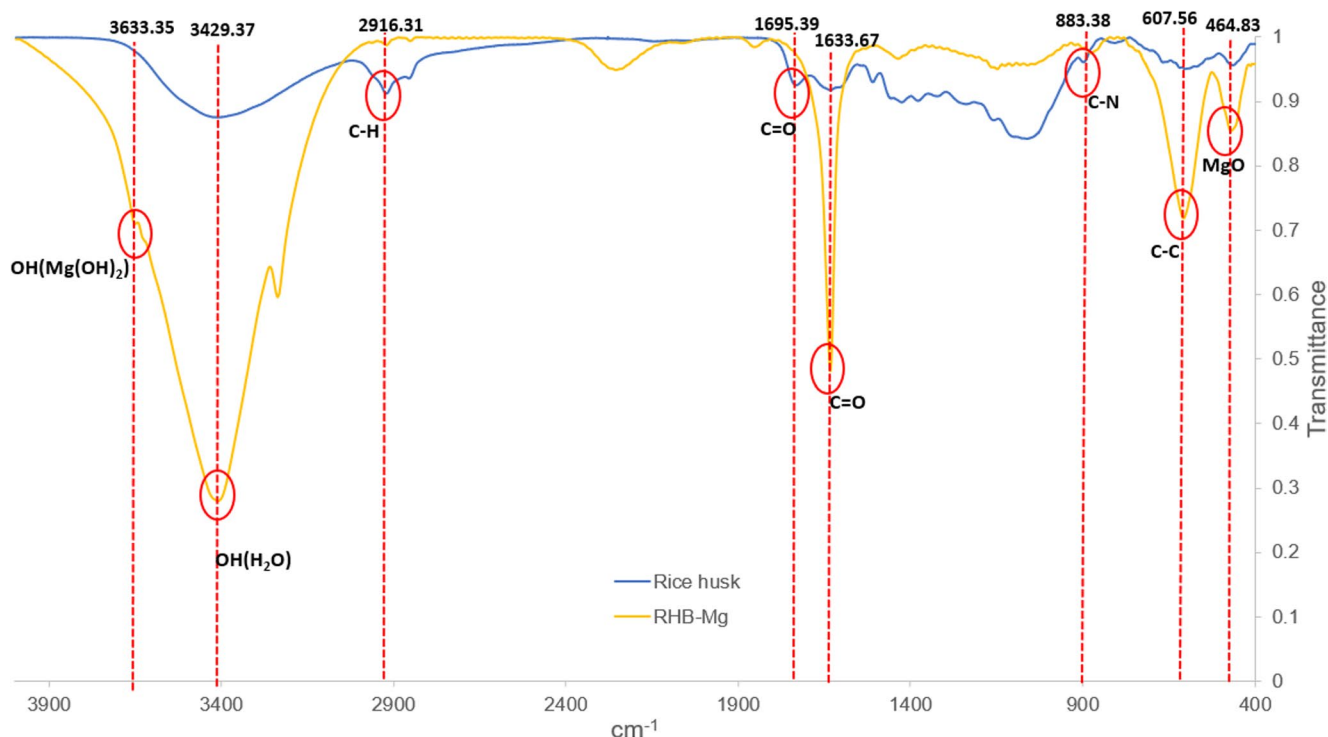


Fig. 2 FTIR of the starting material and RHB-Mg

the rice husk presented bands at 601.78 cm^{-1} , 883.38 cm^{-1} , 1039.61 cm^{-1} , 1695.39 cm^{-1} , 2916.31 cm^{-1} , and 3423.58 cm^{-1} , corresponding to vibrations related to the C-C, C-N, Si-O-Si, C = O, C-H, and OH groups [35, 36], while the RHB-Mg spectra showed bands at 464.83 cm^{-1} , 607.56 cm^{-1} , 873.74 cm^{-1} , 1060.82 cm^{-1} , 1479.37 cm^{-1} , 1633.67 cm^{-1} , 2920.17 cm^{-1} , 3429.37 cm^{-1} , and 3633.35 cm^{-1} , associated with the functional groups MgO, C-C, C = C, Si-O-Si, C = O, OH(H₂O), and OH(Mg(OH)₂) [11, 21, 35]. These results indicate that Mg impregnation occurred, modifying the functional groups of the biochar treated with respect to the untreated biomass. In general, RHB-Mg presented organic functional groups, such as OH, C = O, and C = C, which would benefit the adsorption process [37].

3.1.2 Scanning electron microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDX)

Figure 3 (a, b) shows the SEM results. It can be observed that the untreated rice husk has an outer epidermis with a wavy structure (see Fig. 3(a)), which may be associated with silica particles in the organic matrix [38, 39], as well as cellulose, hemicellulose, and lignin compounds [11, 38]. Meanwhile, the magnesium-modified biochar displayed a more porous structure compared to the precursor material (see Fig. 3(b)). This could be related to the combined effect of pyrolysis temperature and chemical modification with Mg.

On the other hand, Table 1 presents the elemental composition of the untreated rice husk and the magnesium-modified biochar (RHB-Mg) before and after the adsorption

Fig. 3 SEM image: (a) Rice husk, (b) RHB-Mg

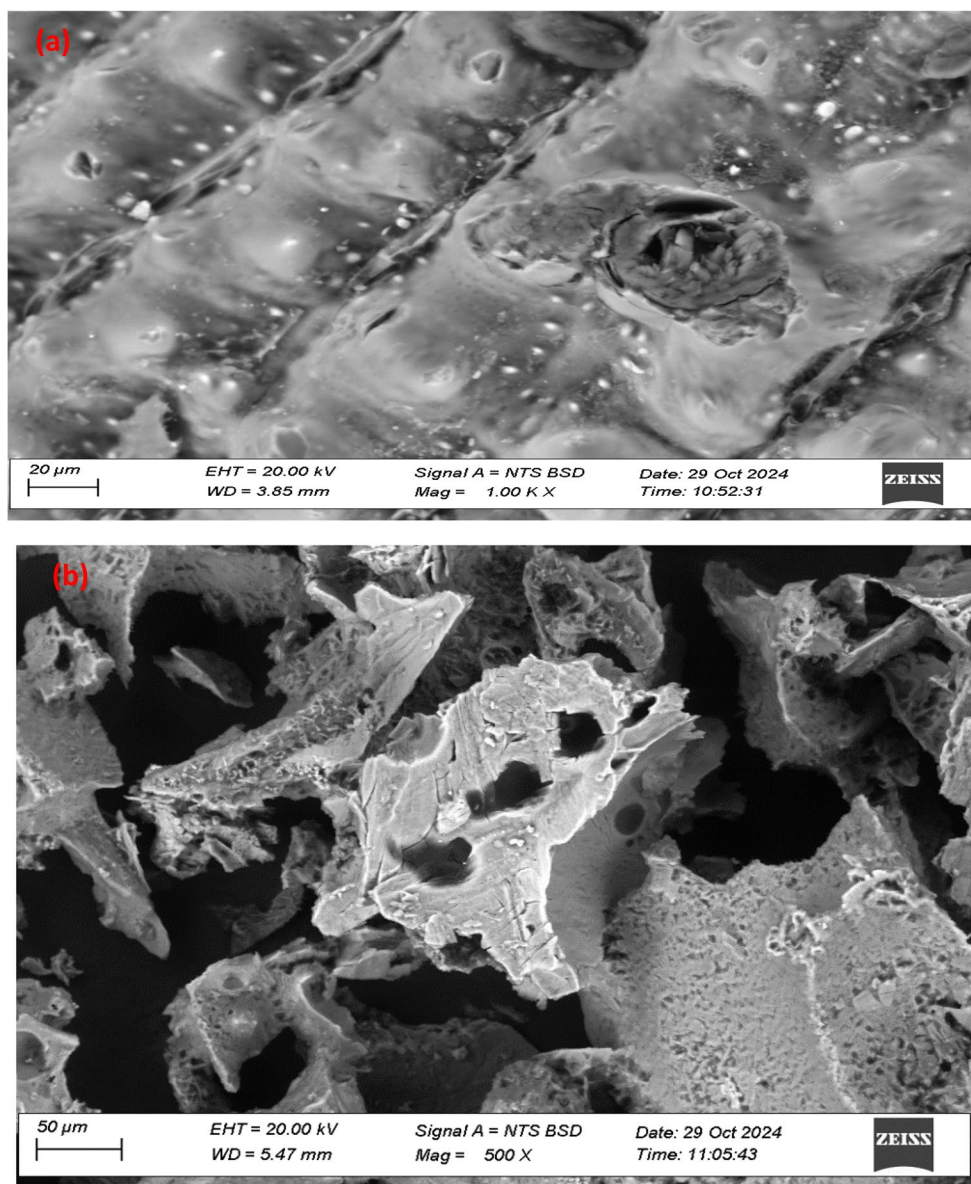


Table 1 Elemental composition and physical properties of the adsorbent

Element	Rice husk	RHB-Mg	RHB-Mg-P	RHB-Mg-N	RHB-Mg-RW
C (%)	26.54	14.54	14.17	16.22	16.46
O (%)	50.06	34.49	26.65	44.10	43.18
Na (%)	-	-	2.88	0.74	2.64
Mg (%)	-	14.24	13.69	26.20	21.57
Al (%)	-	-	-	0.13	-
Si (%)	22.58	5.02	0.25	1.76	3.98
P (%)	-	-	3.12	-	0.16
K (%)	0.21	-	-	-	-
Cl (%)	-	28.6	0.77	0.46	0.61
Cu (%)	-	0.11	0.46	-	0.23
Zn (%)	-	2.49	37.22	10.13	11.10
Ca (%)	-	-	-	-	0.49
S (%)	-	-	-	-	0.05
Total	99.39	99.49	99.21	99.74	99.93
BET surface area (m ² /g)	0.37	18.90	-	-	-
pH _{PZC}	6.70	10.30	-	-	-
Density (g/cm ³)	-	0.20	-	-	-
Average pore size (nm)	-	22.12	-	-	-
Average particle size (mm)	-	0.10	-	-	-

[RHB-Mg]: Rice husk biochar before adsorption. [RHB-Mg-N]: Rice husk biochar after nitrate adsorption in synthetic water. [RHB-Mg-P]: Rice husk biochar after phosphate adsorption in synthetic water. [RHB-Mg-RW]: Rice husk biochar after nitrate and phosphate adsorption in real wastewater

of nitrate and phosphate. It can be observed that RHB-Mg exhibited magnesium concentration compared to the starting material, confirming the impregnation of Mg. It is also noted that after phosphate adsorption, phosphate concentration was detected in RHB-Mg, which was not found in either the starting material or in RHB-Mg before adsorption, confirming phosphate adsorption, as shown in the subsequent sections. Meanwhile, RHB-Mg, after nitrate removal, did not show nitrogen in its structure, possibly because the nitrate removal efficiency was lower than that of phosphate, and a measurable concentration was not reached by the SEM-EDX equipment used.

3.1.3 BET surface area and point of zero charge (pH_{PZC})

The rice husk and RHB-Mg exhibited respective BET surface area values of 0.37 and 18.9 m²/g, respectively (see Table 1). The increase could be associated with the devolatilization of larger biomass particles that occurs during the

rise in pyrolysis temperature, as well as the effect of the Mg modification, leading to a reduction in volatile particles and the release of smaller molecules that enhance the proportion of micropores, thereby increasing the surface area of the materials [40].

Regarding the zero point charge values, the rice husk exhibited a pH_{PZC} value of 6.7, while RHB-Mg showed a pH_{PZC} of 10.3. This could be related to the hydroxyl groups formed during the Mg modification, which tended to impart a more negative charge to RHB-Mg [21, 41].

3.2 Fixed bed adsorption experiments

3.2.1 Effect of flow rate on nitrate and phosphate adsorption

Since the flow rate is a fundamental variable for the design of fixed-bed adsorbents at a real scale, the influence of this parameter on the removal of nitrate and phosphate using RHB-Mg was investigated. The influent concentration of each nutrient was kept constant at 50 mg/L for nitrate and 100 mg/L for phosphate, with the bed height ($Z=4$ cm) also fixed.

Figure 4 (a, b) shows the effect of the flow rate on the breakthrough curves for nitrate and phosphate. It can be observed that as the flow rate increases, the exhaustion of the adsorbent accelerates, leading to a reduction in both the breakthrough time (t_b) and the saturation time (t_s). For the evaluated flow rates ($Q=5.5$ mL/min and $Q=20$ mL/min), increasing the flow rate t_s was reduced from 0.1 to 0.2 min for nitrate and from 9.4 to 2 min for phosphate (see Table 2).

This is because high flow rates of the influent passing through the column quickly occupy the available active adsorption sites for nutrients on the surface of the RHB-Mg bed [42]. Additionally, higher flow rates reduce the hydraulic retention time of the influent in the column, decreasing the contact time between the nutrients and the RHB-Mg. This can also limit the intraparticle diffusion mechanism [43]. Moreover, the breakthrough time in the column was faster for nitrate compared to phosphate (see Table 2). Studies by Najmi et al. [43], Gizaw et al. [42] and Manjunath & Kumar [44] have also observed this behavior.

3.2.2 Effect of initial concentration on nitrate and phosphate adsorption

Considering that the initial concentration of the influent is another key parameter in the design of adsorption columns at an industrial scale, its effect on nitrate and phosphate removal was studied. Two concentrations were evaluated:

Fig. 4 Breakthrough curves for adsorption of: **(a)** Nitrate ($C_0 = 50$ mg/L) and **(b)** Phosphate ($C_0 = 100$ mg/L) (Bed height = 4 cm, $pH \approx 7$, temperature = 20°C)

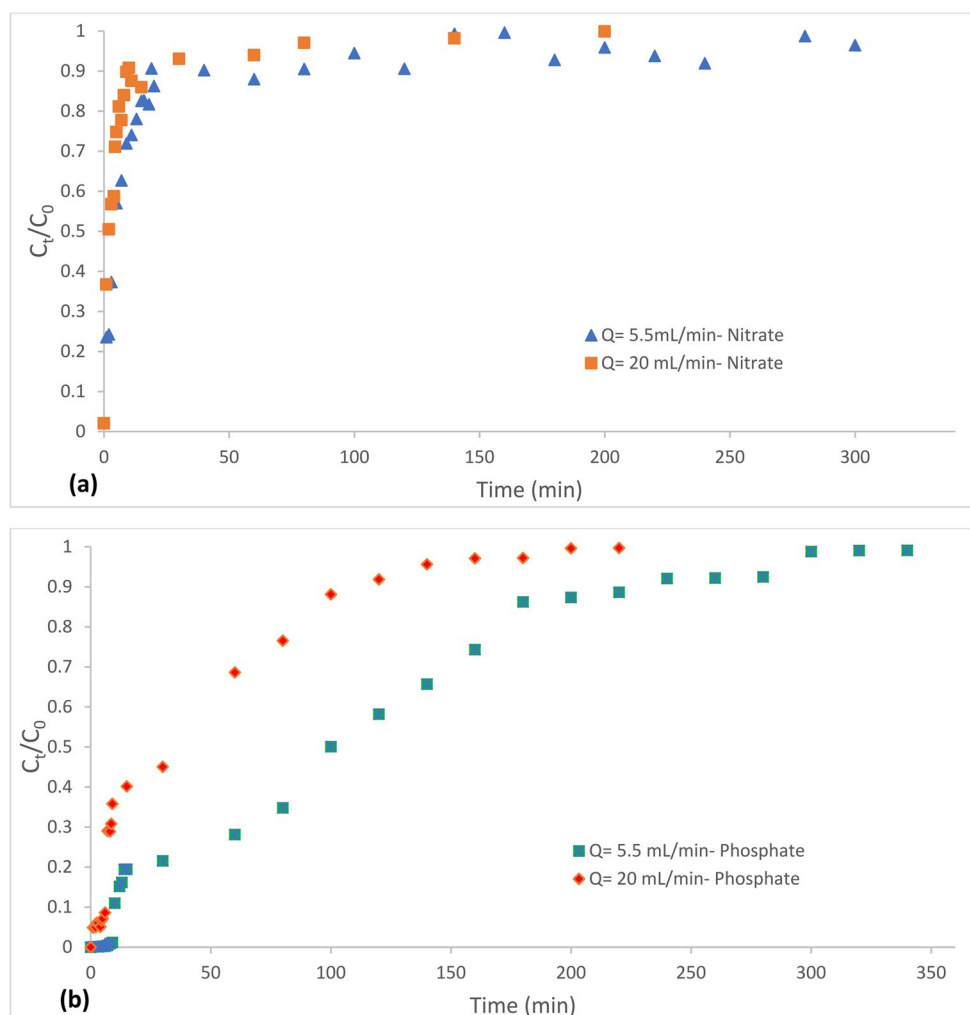


Table 2 Estimation of breakthrough curve parameters by varying flow rates

Pollutant	Q (mL/min)	C_0 (mg/L)	t_b (min)	V_e (mL)	t_s (min)	q_{bed} (mg/g)	E (%)	MTZ (cm)
Nitrate	5.5	50.0	0.2	1258.9	228.9	4.0	7.0	4.0
	20.0	50.0	0.1	1330.2	66.5	5.0	4.0	4.0
Phosphate	5.5	100.0	9.4	1568.9	285.2	45.0	36.0	3.9
	20.0	100.0	2.0	2944.9	147.2	78.0	24.0	3.9

[Q] = Flow rate (mL/min), $[C_0]$ = Influent concentration (mg/L), $[t_b]$ = Breakthrough time (min), $[V_e]$ = Effluent volume (mL), $[t_s]$ Saturation time (min), $[q_{bed}]$ = Adsorption capacity (mg/g), [E] = Efficiency (%), [MTZ] = Mass transfer zone (cm). $pH \approx 7$, Temperature = 20°C , and Bed depth = 4 cm

20 and 30 mg/L for nitrate, and 20 and 50 mg/L for phosphate, while keeping the bed height ($Z = 4$ cm) and flow rate ($Q = 5.5$ mL/min) constant. This flow rate was selected based on the highest removal efficiency of nitrate and phosphate observed in the flow rate variation experiments. The results are shown in Fig. 5 (a, b) and Table 3.

It was found that as the initial concentration increased, the breakthrough curve became steeper. The breakthrough time decreased from 3 to 0.5 min when the initial nitrate concentration increased from 20 to 30 mg/L, and with the

highest concentration analyzed (50 mg/L), the breakthrough time showed the lowest value, 0.2 min; while for phosphate, it decreased from 14 to 11 min when the initial concentration increased from 20 to 50 mg/L, and this time was further reduced to 9.4 min with the highest concentration (100 mg/L). This can be explained by the fact that, as the initial nutrient concentration increases, the active adsorption sites become saturated more quickly due to a higher mass flow of contaminant interacting with the RHB-Mg bed, thus reducing the operational time and adsorption efficiency [45].

Fig. 5 Effect of initial concentration on breakthrough curves for adsorption of: **(a)** Nitrate ($C_0 = 50$ mg/L, 30 mg/L and 20 mg/L) and **(b)** Phosphate ($C_0 = 100$ mg/L, 50 mg/L and 20 mg/L). Bed height = 4 cm, pH (~ 7), Temperature = 20 °C

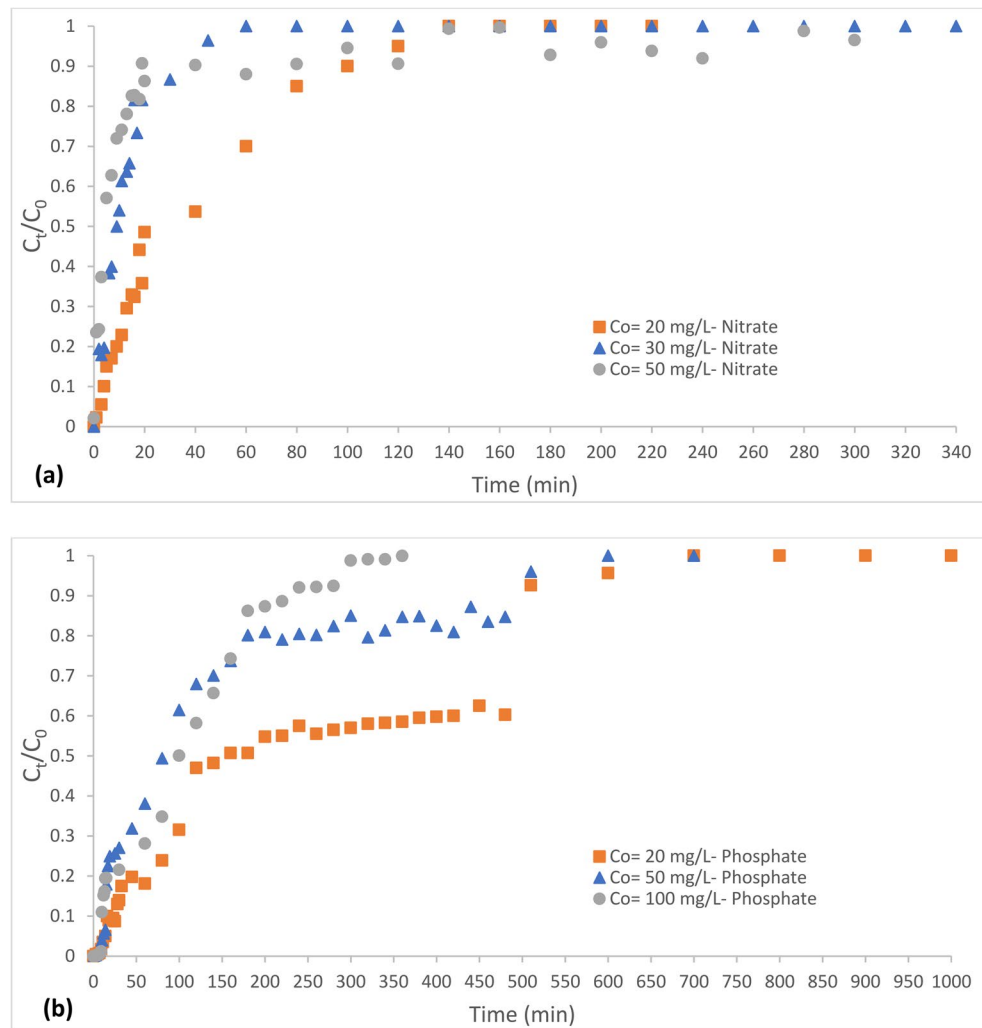


Table 3 Estimation of breakthrough curve parameters by varying the initial concentration of the contaminant

Pollutant	C_0 (mg/L)	t_b (min)	V_e (mL)	t_s (min)	q_{bed} (mg/g)	E (%)	MTZ (cm)
Nitrate	50.0	0.2	1258.9	228.9	4.0	7.0	4.0
	30.0	0.5	1650.0	300.0	1.5	4.0	4.0
	20.0	2.9	1650.0	300.0	2.9	18.0	3.9
Phosphate	100.0	9.4	1568.9	285.2	45.0	36.0	3.9
	50.0	11.3	2790.4	507.3	42.0	30.0	3.9
	20.0	14.0	3300.0	600.0	19.0	31.2	3.9

[C_0] = Influent concentration (mg/L), [t_b] = Breakthrough time (min), [V_e] = Effluent volume (mL), [t_s] Saturation time (min), [q_{bed}] = Adsorption capacity (mg/g), [E] = Efficiency (%), [MTZ] = Mass transfer zone (cm). pH ≈ 7 , Temperature = 20 °C, and Bed depth = 4 cm. Q = 5.5 mL/min, pH ~ 7 , temperature = 20 °C, and bed depth = 4 cm

Additionally, as observed in the study of the flow rate effect, it was also found that the breakthrough time for nitrate adsorption was much faster than that for phosphate adsorption when varying the initial concentration of both contaminants. This can be related to the fact that the removal efficiency for phosphate was higher than that for nitrate (see Table 3), as reported in the study by Najmi et al. [43].

3.2.3 Effect of bed height on nitrate and phosphate adsorption

To improve the adsorption capacity of nitrate and phosphate in a fixed-bed column, the effect of bed depth was evaluated as an operational and design parameter. The results are shown in Fig. 6 (a, b) and Table 4. It was observed that, for all the evaluated bed depths, the bed

Fig. 6 Effect of bed height ($Z = 6$ cm and 8 cm) on breakthrough curves for the adsorption of: (a) Nitrate ($C_0 = 50$ mg/L) and (b) Phosphate (100 mg/L). Flow rate = 5.5 mL/min. pH (~7), temperature = 20°C

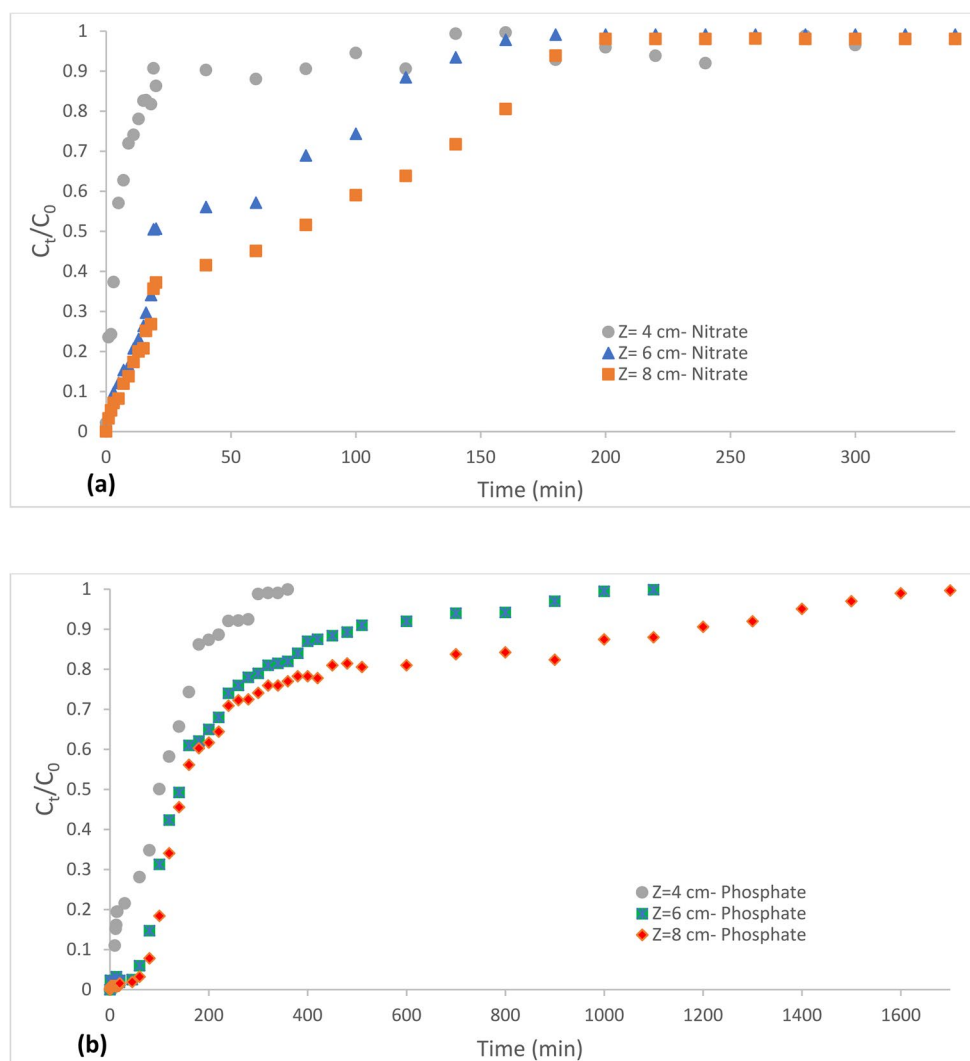


Table 4 Estimation of breakthrough curve parameters by varying the bed height of RHB-Mg

Pollutant	Z (cm)	t_b (min)	V_e (mL)	t_s (min)	q_{bed} (mg/g)	E (%)	MTZ (cm)
Nitrate	4.0	0.2	1258.9	228.9	4.0	7.0	4.0
	6.0	1.7	809.7	147.2	8.2	17.0	5.9
	8.0	1.9	1060.3	192.8	9.4	25.0	7.9
Phosphate	4.0	9.4	1568.9	285.2	45.0	36.0	3.9
	6.0	55.8	4950.0	900.0	51.0	21.0	5.6
	8.0	67.7	8250.0	1500.0	61.0	21.0	7.6

[Z] = Bed depth (cm), [t_b] = Breakthrough time (min), [V_e] = Effluent volume (mL), [t_s] = Saturation time (min), [q_{bed}] = Adsorption capacity (mg/g), [E] = Efficiency (%), [MTZ] = Mass transfer zone (cm). $Q = 5.5$ mL/min, pH ~ 7, temperature = 20 °C, and $C_0 = 50$ mg/L for nitrate and 100 mg/L for phosphate

saturated more quickly when fed with nitrate compared to phosphate, as reported by Gizaw et al. [42].

As the bed depth increased, the saturation time also increased because the active sites of RHB-Mg increased with the bed height, which reduced the hydraulic retention time of the nitrate and phosphate flow, thereby increasing the adsorption capacity of the column [44, 46]. This behavior was similar to those reported by Gizaw et al. [42] and Najmi et al. [43].

The behavior of the adsorption capacity order for nitrate and phosphate remained consistent with the study of other operational variables (flow rate and initial influent concentration). It was observed that the adsorption capacity for phosphate was higher than that for nitrate, in agreement with the results obtained from the batch adsorption experiments.

However, it is important to highlight that the adsorption results could vary depending on the column diameter (D)

and its relationship with the particle diameter (d_p), as a small D/d_p ratio causes the column wall to significantly influence porosity, flow rate, heat transfer, and mass transfer within the bed, which in turn affects the breakthrough curve. For instance, the breakthrough curve could differ at the center of the column compared to its behavior at the wall, potentially impacting the removal of nitrate and phosphate [47].

In this study, a small column (1.86 cm in diameter) was used, a value that falls within the range reported in other studies ($1 < D < 2.8$ cm) [42–44, 48]. According Kwapinski et al. [47] when $D/d_p > 20$, axial dispersion (caused by the wall effect of the column) does not significantly affect breakthrough curves. The column presented a D/d_p ratio of 186, which is higher than the values reported by Kwapinski et al. [47] ($5 < D/d_p < 50$). Based on this criterion, the adsorption of nitrate and phosphate due to wall effects was considered negligible in this study. However, this aspect was not specifically addressed, as it lies beyond the scope of the present work. Therefore, future studies are required to investigate this phenomenon, including the influence of column diameter and its relationship with particle size on the adsorption capacity of nitrate and phosphate, using tools such as mathematical modeling.

On the other hand, in Table 5, RHB-Mg is compared with other adsorbents studied for the removal of nitrate and phosphate through continuous flow adsorption. Adsorption capacities for nitrate lower than the one found in this study (9.4 mg/g) have been reported for other adsorbents: Calcium silicate hydrates (2.13 mg/g) [42], Prosopis juliflora activated carbon (5.5 mg/g) [44], and coconut shell granular activated carbon modified with Zn (7.92 mg/g) [49]. However, other studies have reported higher nitrate removal efficiencies, such as Red mud modified with HCl (34.56 mg/g) [50] and boron waste biochar (123.38 mg/g) [48].

Regarding phosphate, adsorption capacities lower than those found in this study (78 mg/g) using RHB-Mg were reported, such as: Leftover coal (0.33 mg/g) [45], Prosopis juliflora activated carbon (8.21 mg/g) [44], zirconium-loaded okara (16.43 mg/g) [51]. On the other hand, other studies reported better adsorption capacities than those found in this study, such as amine cross-linking biosorbent (103.1 mg/g) [52] and boron waste biochar (108.35 mg/g) [48].

These differences in the adsorption capacities of the examined nutrients could be attributed to: (1) the different

Table 5 Comparison of adsorption capacities with other adsorbents

Adsorbent	BET area (m ² /g)	q _m (mg/g)	Operational variables	Pollutant	Reference
Rice husk biochar modified with Mg (RHB-Mg)	18.9	9.4	C ₀ =20–100 mg/L, Q = 5.5 mL/min, Z = 4 cm, m = 1.6 g, Natural pH = ~ 7, Temperature = 20 °C.	Nitrate	This study
Magnesium-modified bamboo biochar	399	78	Co = 9.98 mg/L, Q = 30 mL/h, m = 1 g, pH = 7.23.	Phosphate	[14]
Calcium silicate hydrates	-	2.13	C ₀ = 25 mg/L nitrate and Co = 5.5 mg/L phosphate, Q = 5–10 mL/min, Z = 6–12 cm, pH = ~ 7	Nitrate	[42]
Prosopis juliflora activated carbon	-	5.61	C ₀ =25–100 mg/L, Q = 8–33 mL/min, Z = 5–15 cm	Phosphate	[44]
Boron waste biochar	30	5.57	C ₀ = 100–200 mg/L, Q = 0.5–1.5 mL/min, Z = 12 cm, pH = 3. Temperature = 25 °C.	Nitrate	[48]
HCl-modified red mud	11.98	123.38	C ₀ = 100–400 mg/L, Q = 15 mL/min, Z = 15 cm, pH = 5.5. Temperature = 25 °C.	Phosphate	[50]
Leftover coal	-	34.56	C ₀ = 10–25 mg/L, Q = 1–2 mL/min, Z = 5–8 cm, pH = 3.5.	Nitrate	[45]
Resin impregnated with iron hydroxide oxides (HFeO)	-	0.33	C ₀ =100 mg/L, Q = 1–2.5 mL/min, Z = 2–6 cm	Phosphate	[53]
Zirconium loaded okara	-	40.67	C ₀ =5.5–15 mg/L, Q = 12–28 mL/min, Z = 11.5–34.5 cm, m = 5–15 g, pH = 3–8	Phosphate	[51]
Zn-modified granular coconut activated carbon	567.52	7.92	C ₀ =10–50 mg/L, Q = 5–20 mL/min, m = 10–30 g, pH = 3. Temperature = 20 °C.	Nitrate	[49]
Amine cross-linking biosorbent	26.27	122.3	C ₀ =50–120 mg/L, Q = 5–10 mL/min, m = 1.2 g	Nitrate	[52]
		103.1		Phosphate	

[q_m]: Adsorption capacity (mg/g), [C₀]: Influent concentration (mg/L), [Q]: Flow rate (mL/min), [Z]: Bed height (cm), [m]: Mass of adsorbent (g)

physicochemical properties of the materials involved, as well as the methods used to prepare these adsorbents; and (2) the different operational variables in the continuous flow adsorption, such as pH, flow rate, bed height, and initial influent concentration, since these affect adsorption. Furthermore, none of the studies reviewed were conducted under the same operational conditions. Therefore, while it may be appropriate to compare different adsorbents while keeping operational variables fixed, this was not the objective of the study.

3.2.4 Study of adsorption with real wastewater

The results of the co-adsorption of nitrate and phosphate from real wastewater using a fixed-bed column with RHB-Mg are shown in Fig. 7 (a, b) and Table 6. The physicochemical characterization values of the real wastewater were specified in Sect. 2.4.4, presenting values of 14.9 mg/L of nitrate, 3.3 mg/L of phosphate, 38.2 mg/L of COD, 30.0 mg/L of alkalinity as CaCO_3 , and a pH of 6.2. It was found that in the adsorption

Fig. 7 Effect of bed height ($Z = 4$ cm and 8 cm) on the break-through curves for adsorption in real wastewater: **(a)** Nitrate ($C_0 = 14.9$ mg/L) and **(b)** Phosphate ($C_0 = 3.3$ mg/L). Flow rate = 5.5 mL/min. pH = 6.2, temperature = 20 °C

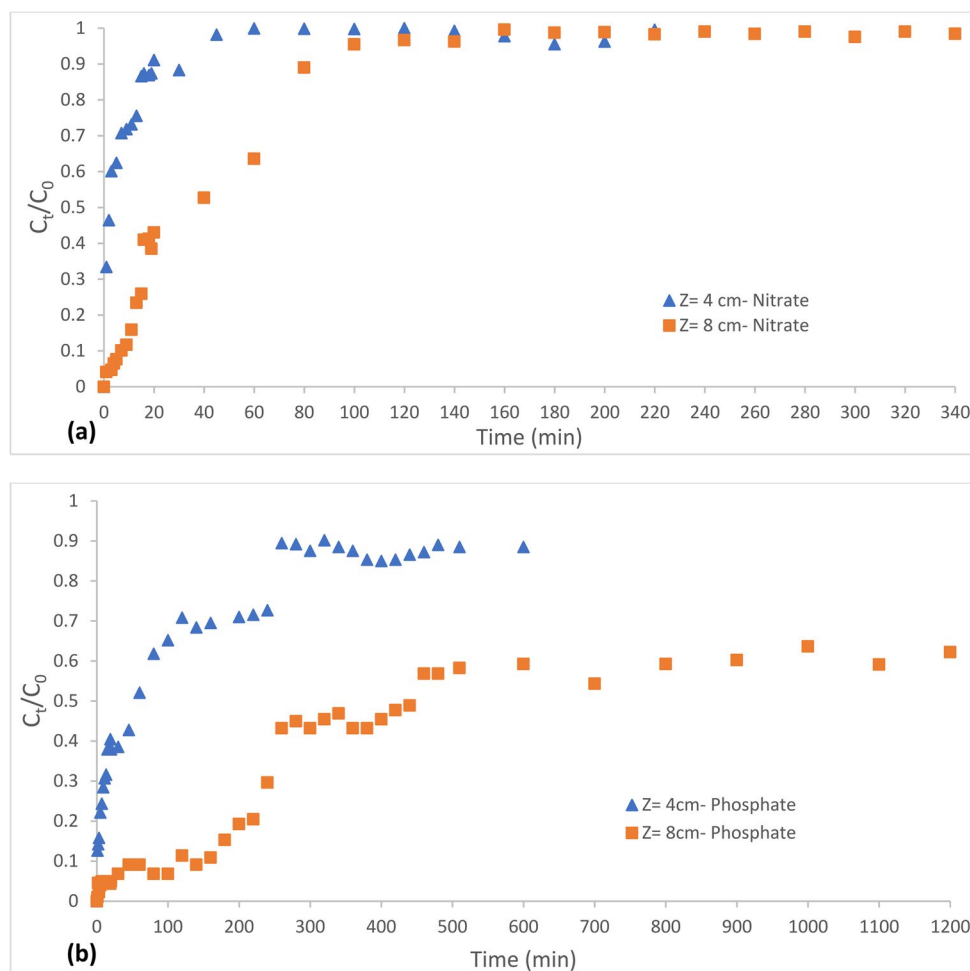


Table 6 Estimation of the breakthrough curve parameters in real wastewater by varying the bed height of RHB-Mg

Pollutant	Z (cm)	t_b (min)	V_e (mL)	t_s (min)	q_{bed} (mg/g)	E (%)	MTZ (cm)
Nitrate	4.0	0.1	220.9	40.2	0.5	5.0	4.0
	8.0	3.2	647.6	117.7	1.4	14.0	7.8
Phosphate	4.0	0.4	3300.0	600.0*	1.8	26.0	4.0
	8.0	20.3	6600.0	1200.0*	2.4	54.5	7.9

[Z]=Bed depth (cm), [t_b]= Breakthrough time (min), [V_e]= Effluent volume (mL), [t_s]= Saturation time (min), [q_{bed}]= Adsorption capacity (mg/g), [E]= Efficiency (%), [MTZ]= Mass transfer zone (cm). $Q = 5.5$ mL/min, pH = 6.2, temperature = 20 °C, and $C_0 = 14.9$ mg/L for nitrate and 3.3 mg/L for phosphate. [*]= t_{oper} (he saturation time was not reached)

time intervals analyzed, C_t/C_0 ranged between 0.9 and 0.99 close to the saturation of RHB-Mg. However, an exception was observed in phosphate adsorption at a bed height of 8 cm, where saturation was not reached, as C_t/C_0 remained around 0.55, similar to the behavior reported by Gizaw et al. [42]. Therefore, further evaluation of different variable ranges, such as flow rates and contact times, is necessary to determine whether full saturation of RHB-Mg can be achieved.

However, the main reason why saturation was not reached in the phosphate adsorption could be related to the fact that competitive adsorption with nitrate and other anions present in the wastewater may have reduced the active sites for phosphate adsorption [54] requiring longer adsorption times (than those studied in the present research) to achieve RHB-Mg saturation. Additionally, the presence of alkalinity and sulfate (not determined in the wastewater sample, but observed in the characterization of the adsorbent after adsorption, where an increase in sulfur content was noted, indicating that the adsorbent removed this chemical element associated with sulfate) in the wastewater (Table 1) may have reduced the adsorption capacity for nitrate and phosphate [42], thus affecting the saturation time of the adsorbent, as described previously.

On the other hand, the maximum adsorption capacity found was 1.4 mg/g for nitrate and 2.4 mg/g for phosphate, both values obtained when operating with the greater bed depth (8 cm), consistent with the results obtained with synthetic water, regarding the effect of bed depth on adsorption in the column.

Furthermore, the break and saturation times, as well as the adsorption efficiency, increased with the increase in bed depth, making it an important variable for the design of nutrient removal from the real wastewater studied. However, it must be selected carefully, considering that increasing the depth increases the energy requirements of the system due to the increase in flow resistance and pressure drop in the fixed-bed column [55].

3.2.5 Fixed bed modelling

To determine the dynamics and kinetic parameters of the fixed-bed adsorption process, mathematical modeling was performed by fitting the studied mathematical models through nonlinear regression of the experimental adsorption data from the column.

The results presented in Table 7; Figs. 8 (a, b, c, d, e, f), 9 (a, b, c, d, e, f), and 10 (a, b, c, d), demonstrate generally good model fits to the experimental column adsorption data ($R^2 \geq 0.9$). However, an exception was observed in the modeling of phosphate adsorption from real wastewater,

Table 7 Modeling of the breakthrough curves for the removal of nitrate and phosphate using RHB-Mg

Pollutant	Conditions				Thomas				Yoon-Nelson				Adam's Bohart				Clark	
	C ₀	Q	Z	q ₀	k _{Th}	R ²	RSME	k _{YN}	T	R ²	RSME	k _{AB}	N ₀	R ²	RSME	A	r	
Nitrate (synthetic water)	50	5.5	4.0	1.05	4.14	0.92	0.07	0.20	6.92	0.91	0.08	0.0041	30634.61	0.92	0.07	7.77	0.23	
	50	20.0	4.0	1.77	8.12	0.92	0.07	0.41	2.83	0.92	0.07	0.0081	14968.61	0.92	0.07	6.73	0.45	
	50	5.5	6.0	7.10	0.50	0.95	0.08	0.03	47.70	0.95	0.08	0.0005	308238.90	0.95	0.08	12.06	0.04	
	50	5.5	8.0	8.90	0.33	0.96	0.07	0.02	79.70	0.96	0.07	0.0003	515074.60	0.96	0.07	14.97	0.03	
Nitrate (real wastewater)	30	5.5	4.0	1.01	6.46	0.98	0.04	0.19	9.77	0.98	0.04	0.0065	29299.78	0.98	0.04	17.13	0.23	
	20	5.5	4.0	2.41	2.47	0.96	0.07	0.05	35.12	0.96	0.07	0.0025	70242.88	0.96	0.07	14.56	0.06	
	14.9	5.5	4.0	0.20	13.24	0.88	0.08	0.18	4.29	0.88	0.08	0.0100	5790.61	0.88	0.08	4.27	0.19	
	14.9	5.5	8.0	1.10	3.06	0.97	0.07	0.05	37.19	0.97	0.07	0.0031	63086.11	0.97	0.07	18.80	0.06	
Phosphate (synthetic water)	100	5.5	4.0	41.64	0.20	0.97	0.06	0.02	121.14	0.97	0.06	0.0002	1219430.98	0.97	0.06	39.09	0.02	
	100	20.0	4.0	17.82	0.36	0.94	0.09	0.04	51.83	0.94	0.09	0.0004	518262.28	0.94	0.09	17.93	0.04	
	100	5.5	6.0	39.70	0.15	0.96	0.09	0.02	173.02	0.96	0.09	0.0002	1219430.90	0.91	0.13	50.34	0.02	
	100	5.5	8.0	34.20	0.13	0.92	0.13	0.01	198.90	0.92	0.13	0.0002	1224591.61	0.84	0.19	45.18	0.02	
Phosphate (real wastewater)	50	5.5	4.0	18.37	0.36	0.89	0.11	0.02	106.86	0.89	0.11	0.0004	518262.28	0.89	0.11	19.49	0.02	
	20	5.5	4.0	18.37	0.34	0.90	0.11	0.01	267.22	0.90	0.11	0.0003	518262.28	0.90	0.11	15.99	0.01	
	3.3	5.5	4.0	1.00	3.14	0.88	0.10	0.01	91.27	0.88	0.10	0.0030	28843.60	0.88	0.10	5.25	0.01	
	3.3	5.5	8.0	2.00	1.65	0.74	0.14	0.00	570.81	0.74	0.14	0.0016	115305.22	0.74	0.14	17.87	0.00	

C₀ (mg/L), Z (cm), Q (mL/min), q₀ (mg/g), k_{Th} (mL min⁻¹ mg⁻¹), k_{YN} (min⁻¹), T (min), k_{AB} (L mg⁻¹ min⁻¹), N₀ (mg/L), A (dimensionless), r (min⁻¹), pH ~ 7, temperature = 20 °C

C_0 (mg/L), Z (cm), Q (mL/min), q_0 (mg/g), k_{Th} (mL min⁻¹ mg⁻¹), k_{YN} (min⁻¹), k_{AB} (L mg⁻¹ min⁻¹), N_0 (mg/L), A (dimensionless), r (min⁻¹), pH ~ 7, temperature = 20 °C

where saturation was not reached within the evaluated time interval. Since breakthrough curve models typically conclude with saturation, the absence of experimental saturation reduced the goodness of fit.

– Thomas model

The parameters of the Thomas model, adsorption capacity q_0 (mg/g) and the reaction rate constant k_{Th} ($\text{mL min}^{-1} \text{mg}^{-1}$), were estimated (see Table 7). For nitrate and phosphate, k_{Th} increased with the flow rate, which can be attributed to the fact that higher flow accelerates the rate of the adsorbate, enhancing the mass transfer and resulting in an increase in k_{Th} [44]. Meanwhile, for both contaminants, k_{Th} decreased when the concentration dropped from 30 to 20 mg/L for nitrate and from 50 to 20 mg/L for phosphate. However, the opposite occurred when the higher concentrations of nitrate (50 mg/L) and phosphate (100 mg/L) were used. Additionally, k_{Th} decreased in all cases with the increase in bed depth, which can be explained by the fact that the concentration gradient created at the surface of RHB-Mg acted as the driving force for adsorption, thereby improving the adsorption capacity [56].

On the other hand, the q_0 results did not follow the trend of decreasing with the increase in flow rate for nitrate, as found in Najmi et al. [43] and Manjunath & Kumar [44], unlike the results reported by Gizaw et al. [42]. This can be attributed to the fact that increasing the flow rate shortens the contact time between the adsorbent and adsorbate, thereby reducing the adsorption capacity, as occurred with phosphate, where the adsorption capacity increased when the flow rate was reduced. Meanwhile, when the adsorbate concentration was reduced, the adsorption capacity tended to improve for both nitrate and phosphate, which is not a usual trend, since increasing the concentration typically enhances the adsorption capacity by increasing the concentration gradient as the driving force for mass transfer [44].

However, the discrepancies found regarding the effect of flow rate and concentration on the expected values of both Thomas model parameters may be associated with the fact that tap water, rather than pure water, was used, which contained nitrate and phosphate in a binary solution. These contaminants could have affected the adsorption dynamics in the column, as water quality parameters change over time, and it has been found that the competition between these ions influences the model parameters [42, 44]. However, this study did not design experiments to determine this phenomenon. This could explain why the adsorption capacities obtained from the breakthrough curves and the Thomas model differ, as has also been reported in other studies [44, 45, 53].

– Yoon and Nelson model

The parameters of the Yoon-Nelson model were estimated, including the Yoon-Nelson rate constant k_{YN} (min^{-1}) and the time required to reach 50% saturation τ (min). It was found that k_{YN} tended to increase and τ decreased as the flow rate increased. This is because, as the adsorbates pass more quickly through the bed, RHB-Mg became saturated more rapidly, causing the rate constant (k_{YN}) to increase, and the time required to reach 50% saturation (τ) to decrease as the adsorbent became exhausted more quickly [57].

On the other hand, for the increase in initial concentrations of nitrate and phosphate, k_{YN} increased and τ tended to decrease. This can be explained according to the idea of Gouran-Orimi et al. [58], who suggested that higher concentrations increase the mass transfer of the evaluated nutrients, leading to faster saturation of the bioadsorbent bed. This results in an increase in the rate constant (k_{YN}) and a decrease in the time to reach 50% exhaustion of the adsorbent (τ).

Regarding the variation in bed depth, for both contaminants, when the height of RHB-Mg increased, k_{YN} decreased and τ increased. This indicates that with greater bed depth, the number of active sites on RHB-Mg increases, improving the adsorption capacity in the fixed bed column [42, 44].

– Bohart-Adams model

The Bohart-Adams model was applied to determine the column saturation concentration N_0 (mg/L) and the kinetic rate constant k_{AB} ($\text{L mg}^{-1} \text{min}^{-1}$). For both contaminants evaluated, N_0 and k_{AB} tended to increase with the flow rate, as the adsorbent becomes loaded more quickly with nitrate and phosphate, which allows N_0 to increase, indicating that the adsorption kinetics were controlled by the external mass transfer in the column adsorption process [57]. Regarding bed depth, when it increased in the adsorption of nitrate and phosphate, N_0 increased and k_{AB} decreased, showing a behavior similar to the results reported by He et al. [57] and Nguyen et al. [51].

On the other hand, the general trend of k_{AB} and N_0 with respect to the variation in the initial concentration was not clear. This could be attributed to the previously mentioned explanation: the influent water quality was not controlled, as tap water was used. This likely influenced the observed behavior.

– Clark model

The parameters A (dimensionless) and r (min^{-1}) of the Clark model were estimated, and it was found that with an increase in flow rate, A tended to decrease, while r tended

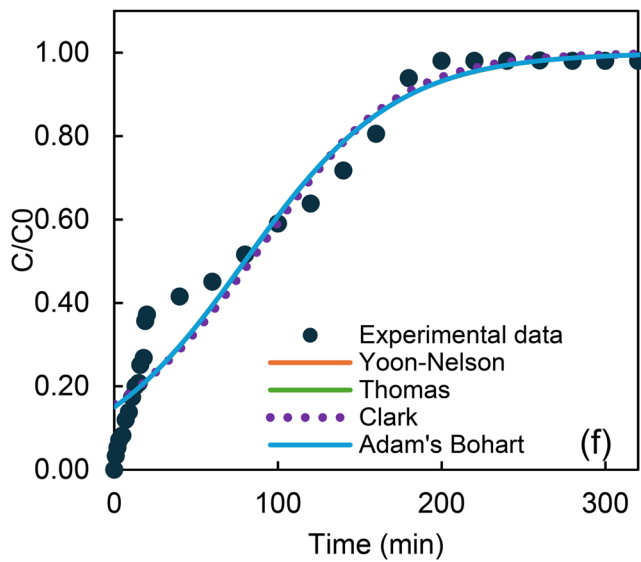
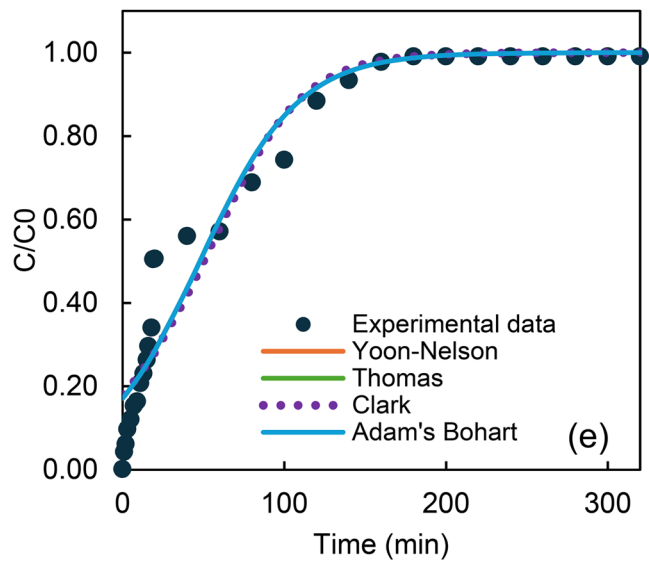
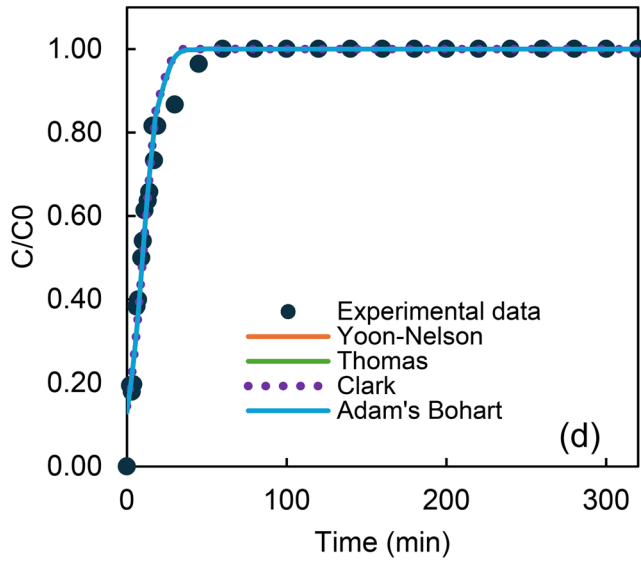
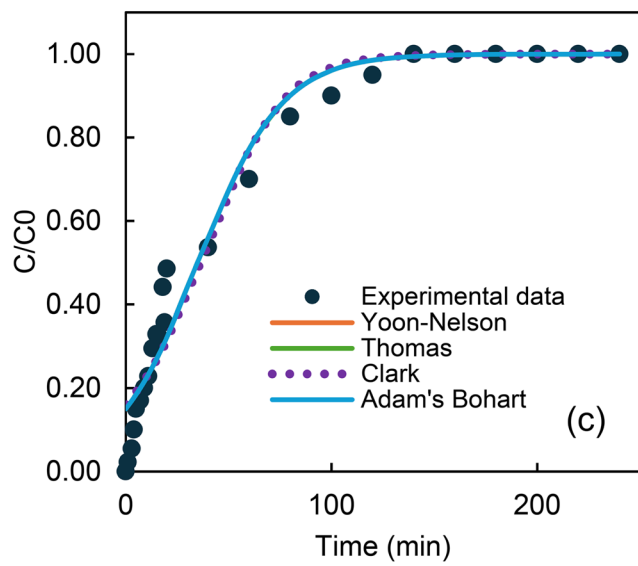
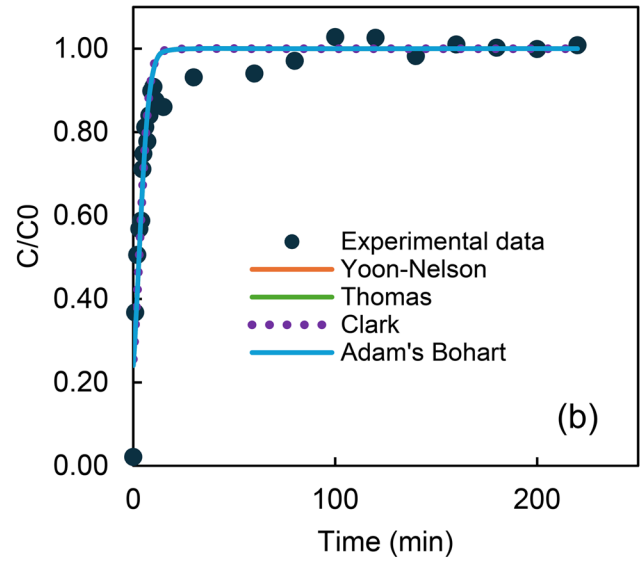
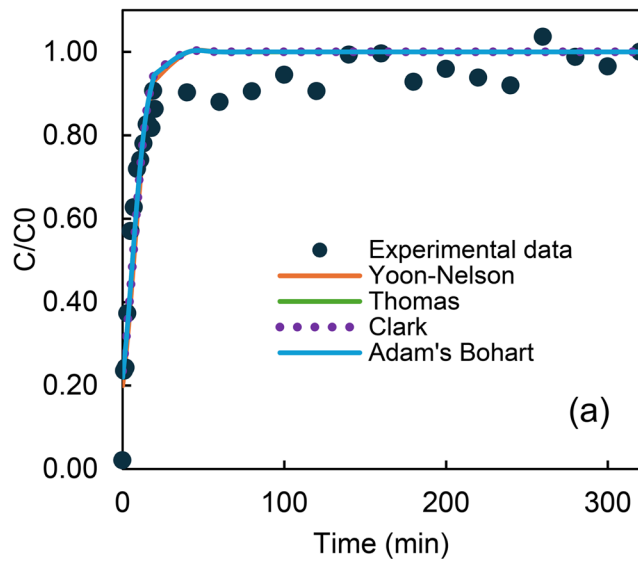


Fig. 8 Graph of breakthrough curve models for nitrate adsorption using RHB-Mg in synthetic water: (a) $C_0 = 50$ mg/L, $Z = 4$ cm, $Q = 5.5$ mL/min. (b) $C_0 = 50$ mg/L, $Z = 4$ cm, $Q = 20$ mL/min. (c) $C_0 = 20$ mg/L, $Z = 4$ cm, $Q = 5.5$ mL/min. (d) $C_0 = 30$ mg/L, $Z = 4$ cm, $Q = 5.5$ mL/min. (e) $C_0 = 50$ mg/L, $Z = 6$ cm, $Q = 5.5$ mL/min. (f) $C_0 = 50$ mg/L, $Z = 8$ cm, $Q = 5.5$ mL/min. pH (~ 7), temperature = 20°C

to increase. This can be explained by the idea presented by Rout et al. [59], which suggests that when the volumetric flow increases, the diffusion distance in the stationary water layers surrounding the adsorbent particles is reduced, thereby intensifying the mass transfer rate (r).

However, with an increase in concentration, the behavior was not well-defined, similar to the results obtained from the application of the Bohart-Adams model, as discussed earlier. No clear trend was observed for the parameters of the models applied to the adsorption of nitrate and phosphate from RHB-Mg. Nevertheless, in general, good model fits were obtained, which accurately describe the breakthrough curves.

3.2.6 Adsorption mechanisms of nitrate and phosphate

Nitrate adsorption may have been governed by multiple interactions, including fixation through ionic bonding with exchangeable cations derived from MgCl_2 in RHB-Mg, as well as electrostatic attraction between nitrate ions and the positively charged bioadsorbent surface in aqueous solution at pH ≈ 7 , which is lower than the point of zero charge ($\text{pH}_{\text{PZC}} = 10.3$) [41, 60].

Regarding phosphate adsorption it is likely associated with: (1) electrostatic attraction between phosphate anions and positively charged RHB-Mg; (2) the presence of MgO and $\text{Mg}(\text{OH})_2$ in RHB-Mg, which can release Mg^{2+} into the aqueous solution and subsequently react with phosphate to form Mg-P precipitates such as $\text{Mg}(\text{H}_2\text{PO}_4)_2$, MgHPO_4 , and/or $\text{Mg}_3(\text{PO}_4)_2$ [21, 41]; (3) complexation of phosphorus with surface functional groups of the adsorbent, such as $\text{C}=\text{O}$ and $-\text{OH}$, which enhances phosphate removal [61]; and (4) ion exchange and ligand exchange processes, which may also occur during phosphate adsorption [62]. Nevertheless, further investigations are required to more accurately elucidate the mechanisms involved in nitrate and phosphate removal by RHB-Mg, using advanced analytical techniques such as X-ray photoelectron spectroscopy (XPS), among others.

3.2.7 Scale-up design

The data obtained from the breakthrough curve with real wastewater were used to scale the adsorption process of nitrate and phosphate to a flow rate of 0.05 L/s (4.32 m³/d), a value that falls within the typical range for

technical-economic analysis studies [63], which is proposed as a future study in this research. These values can be scaled using the scale-up approach, as there is similarity between the hydraulic retention time and the hydrodynamic characteristics between the small-scale fixed-bed column adsorption process and the pilot or full-scale process [64]. The starting data for scaling the fixed-bed column adsorption process are summarized in Table 8:

The adsorption rate (FR) of the column with circular geometry was calculated using Eq. (16):

$$FR = \frac{Q_{ss}}{A_{ss}} = \frac{4Q_{ss}}{\pi D_{ss}^2} \quad (16)$$

Where: [Q_{ss}] = flow rate of the small-scale column, [A_{ss}] = cross-sectional area of the small-scale column, [D_{ss}] = diameter of the small-scale column.

The cross-sectional area of the large-scale column (A_{LS}) was determined using Eq. (17)

$$A_{LS} = \frac{Q_{LS}}{FR} \quad (17)$$

Where: [Q_{LS}] = flow rate of the large-scale column. The bed volume of the large-scale column ($V_{b,LS}$) was estimated using Eq. (18):

$$V_{b,LS} = A_{LS}H_{LS} \quad (18)$$

Where: [H_{LS}] = depth or height of the bed in the large-scale column. The hydraulic retention time (HRT) in the column is calculated using Eq. (19):

$$HRT = \frac{V_{b,LS}}{Q_{LS}} \quad (19)$$

Based on the design conditions, for a flow rate of 4.32 m³/d, a column diameter of 43.44 cm and a column volume of 30 L were estimated for scaling-up to the adsorption process, for a hydraulic retention time of approximately 10 min for the adsorption of nitrate and phosphate using RHB-Mg (Table 9). It was estimated that a bed depth of 20 cm would be required to maintain an adsorption rate of 2.02 cm/min for nitrate and phosphate with the characteristics of the real wastewater studied.

However, the design characteristics will change depending on the physicochemical characteristics of the influent, as well as the operational variables required for the optimization of the nitrate and phosphate adsorption process. For operational reasons, it is recommended to set up the adsorption system with at least two sets of columns operated in parallel, where each of these could, for example, operate

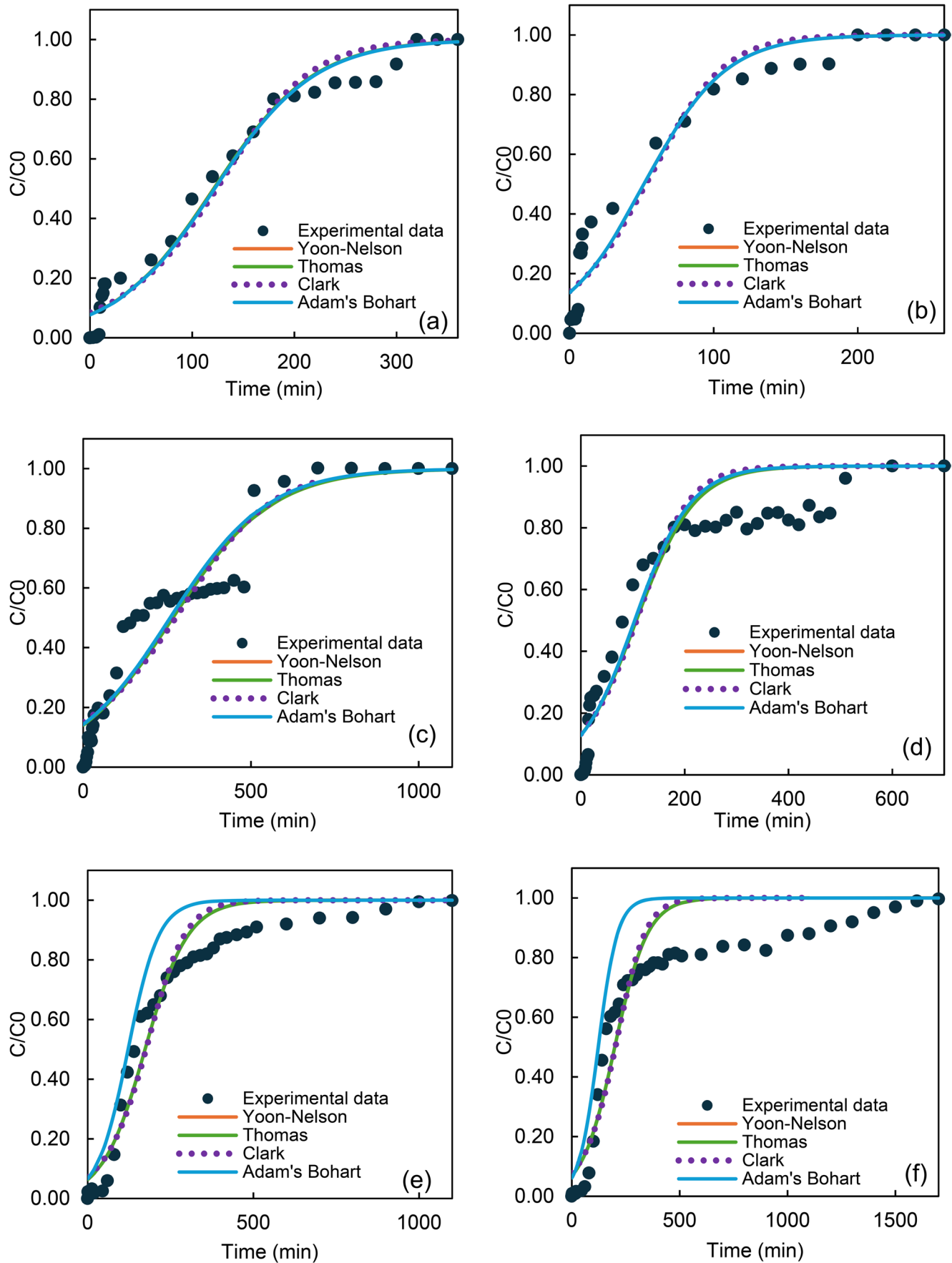


Fig. 9 Graph of breakthrough curve models for phosphate adsorption using RHB-Mg in synthetic water: (a) $C_0 = 100$ mg/L, $Z = 4$ cm, $Q = 5.5$ mL/min, (b) $C_0 = 100$ mg/L, $Z = 4$ cm, $Q = 20$ mL/min, (c) $C_0 = 20$ mg/L, $Z = 4$ cm, $Q = 5.5$ mL/min, (d) $C_0 = 50$ mg/L, $Z = 4$ cm, $Q = 5.5$ mL/min, (e) $C_0 = 100$ mg/L, $Z = 6$ cm, $Q = 5.5$ mL/min, (f) $C_0 = 100$ mg/L, $Z = 8$ cm, $Q = 5.5$ mL/min. pH (~ 7), temperature = 20°C

with 2 or more adsorption units in series, in order to prolong the duration of the process before the saturation of the bio-adsorbent (RHB-Mg) [61].

Nevertheless, these scaling results constitute an important tool for assessing techno-economic and environmental performance by using economic indicators and evaluating the environmental impact of the process through Life Cycle

Assessment (LCA). This approach allowed the determination of the economic and environmental feasibility of nutrient adsorption from real wastewater using the proposed biochar, as well as the reuse of the spent adsorbent material as a soil amendment in crop cultivation (unpublished data).

4 Conclusions

Biochar modified with Mg was produced from rice husk for the removal of nitrate and phosphate from both synthetic and real wastewater in a fixed-bed column. Its physicochemical properties were characterized and compared

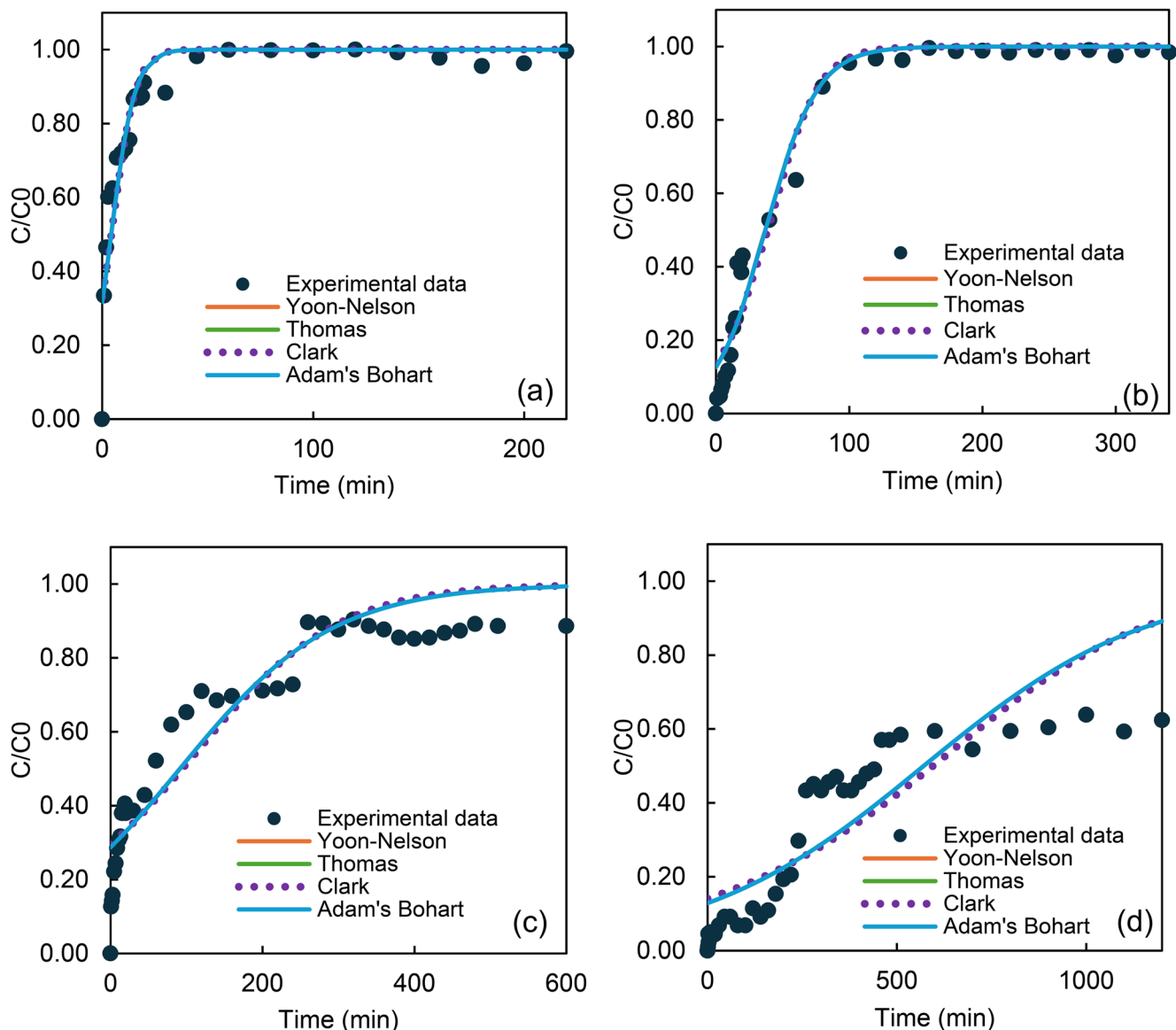


Fig. 10 Graph of breakthrough curve models for nitrate and phosphate adsorption using RHB-Mg in real wastewater: (a) $C_0 = 14.9$ mg/L nitrate and $Z = 4$ cm, (b) $C_0 = 14.9$ mg/L nitrate and $Z = 8$ cm, (c) $C_0 =$

3.3 mg/L phosphate and $Z = 4$ cm, (d) $C_0 = 3.3$ mg/L phosphate and $Z = 8$ cm. $Q = 5.5$ mL/min, pH = 6.2 , temperature = 20°C

Table 8 Small-scale column adsorption study data

Variable	Value	Unit
Small-scale column flow rate (Qss)	5.5	mL/min
Small-scale bed depth (Hss)	8	cm
Small-scale column internal diameter (Dss)	1.86	cm
Small-scale column height (hss)	12.5	cm
Initial nitrate concentration (CoN)	14.9	mg/L
Initial phosphate concentration (CoP)	3.3	mg/L
Nitrate breakthrough concentration (LMP, N)	10	mg/L
Phosphate breakthrough concentration (LMP, P)	0.5	mg/L

[LMP]: Maximum permissible limit established by environmental regulations

Table 9 Design parameters for scaling up the nitrate and phosphate removal process

Parameter	Value	Equation used
Large-scale column flow rate, Q_{LS} (m ³ /d)	4.32	-
Adsorption rate, FR (cm/min)	2.02	(16)
Large-scale column cross-sectional area, A_{LS} (m ²)	0.15	(17)
Large-scale column diameter, D_{LS} (cm)	43.44	(16)
Large-scale bed volume, $V_{b,LS}$ (L)	30	(18)
Hydraulic retention time, HRT (min)	10	(19)
Large-scale bed depth, H_{LS} (cm)	20 cm	(18)

with those of the raw material (unmodified rice husk) to assess the transformations resulting from pyrolysis followed by chemical modification with magnesium chloride. FTIR analysis revealed the presence of MgO, OH(H₂O), and OH(Mg(OH)₂) functional groups in the modified biochar, which may have enhanced chemical adsorption, particularly for phosphate. Adsorption capacities of 9.4 mg/g for nitrate and 78 mg/g for phosphate were obtained, which could be considered significant when compared to other studies. Overall, the adsorption performance for phosphate was markedly higher than that for nitrate, with an adsorption capacity approximately eight times greater, demonstrating a stronger affinity of Mg-modified biochar toward phosphate species. This suggests that RHB-Mg could be considered as an alternative for the treatment of water contaminated with these nutrients using adsorption columns, given its high nitrate and phosphate removal efficiency, which allows compliance with regulatory limits when discharged into surface water bodies. For example, effluent concentrations lower than the maximum permissible limits established by Colombian regulations (10 mg/L for nitrate and 0.5 mg/L for phosphate) were achieved using the proposed adsorption process, thereby preventing the eutrophication of water bodies. Since no pH adjustment is required, the process is more cost-effective by lowering chemical expenses associated with adsorption. Additionally, using

RHB-Mg at ambient temperature eliminates the need for energy input to raise the influent temperature, further reducing operational costs. The four models evaluated (Thomas, Bohart-Adams, Yoon-Nelson, and Clark) generally fitted the experimental data well ($R^2 \approx 0.9$), studying the impact of flow rate, influent concentration, and bed depth on the fixed-bed column adsorption process. The study of these variables could be applied to scale up the column adsorption process to an industrial scale for water contaminated with these two nutrients.

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Data availability All relevant data are included in the paper.

Declarations

Ethical approval Is not applicable.

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Competing interests The authors declare no competing interests.

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References

1. von Sperling M (2016) Urban Wastewater Treatment in Brazil. Washington, D. C
2. Akinawo SO (2023) Eutrophication: Causes, consequences, physical, chemical and biological techniques for mitigation strategies. Environ Challenges 12:100733. <https://doi.org/10.1016/j.nvc.2023.100733>
3. Kumar PS, Korving L, van Loosdrecht MCM, Witkamp G-J (2019) Adsorption as a technology to achieve ultra-low concentrations of phosphate: Research gaps and economic

- analysis. *Water Res X* 4:100029. <https://doi.org/10.1016/j.wroa.2019.100029>
4. Lugo-Arias J, Vargas SB, Maturana A et al (2024) Nutrient Removal from Aqueous Solutions Using Biosorbents Derived from Rice and Corn Husk Residues: A Systematic Review from the Environmental Management Perspective. *Water (Basel)* 16:1543. <https://doi.org/10.3390/w16111543>
 5. Vargas SB, Lugo-Arias J, Tarazona HDF et al (2024) Chemical and microbiological pollution removal coupled with biomass production using native microalgal-bacterial consortia from moderate and highly polluted water bodies. *Algal Res* 77:103335. <https://doi.org/10.1016/j.algal.2023.103335>
 6. Shukla N, Sahoo D, Remya N (2019) Biochar from microwave pyrolysis of rice husk for tertiary wastewater treatment and soil nourishment. *J Clean Prod* 235:1073–1079. <https://doi.org/10.1016/j.jclepro.2019.07.042>
 7. Rout PR, Shahid MK, Dash RR et al (2021) Nutrient removal from domestic wastewater: A comprehensive review on conventional and advanced technologies. *J Environ Manage* 296:113246. <https://doi.org/10.1016/j.jenvman.2021.113246>
 8. FAO (2024) Food Outlook – Biannual report on global food markets. FAO
 9. IPCC (2007) Climate Change 2007: the physical science basis. Contribution of working group I to the Fourth Assessment Report of the Intergovernmental Panel Climate Change. Cambridge University Press
 10. Schofield HK, Pettitt TR, Tappin AD et al (2019) Biochar incorporation increased nitrogen and carbon retention in a waste-derived soil. *Sci Total Environ* 690:1228–1236. <https://doi.org/10.1016/j.scitotenv.2019.07.116>
 11. Konneh M, Wandera SM, Murunga SI, Raude JM (2021) Adsorption and desorption of nutrients from abattoir wastewater: modelling and comparison of rice, coconut and coffee husk biochar. *Heliyon* 7:e08458. <https://doi.org/10.1016/j.heliyon.2021.e08458>
 12. Fatima I, Ahmad M, Vithanage M, Iqbal S (2021) Abstraction of nitrates and phosphates from water by sawdust- and rice husk-derived biochars: Their potential as N- and P-loaded fertilizer for plant productivity in nutrient deficient soil. *J Anal Appl Pyrol* 155:105073. <https://doi.org/10.1016/j.jaap.2021.105073>
 13. Lugo-Arias J, González-Álvarez J, Maturana A et al (2025) Removal of Nitrate and Phosphate from aqueous solutions using bioadsorbents derived from agro-industrial wastes of rice husk and corn stalk. *Biomass Convers Biorefin*. <https://doi.org/10.1007/s13399-025-06720-4>
 14. Jiang D, Chu B, Amano Y, Machida M (2018) Removal and recovery of phosphate from water by Mg-laden biochar: Batch and column studies. *Colloids Surf Physicochem Eng Asp* 558:429–437. <https://doi.org/10.1016/j.colsurfa.2018.09.016>
 15. Alhashimi HA, Aktas CB (2017) Life cycle environmental and economic performance of biochar compared with activated carbon: A meta-analysis. *Resour Conserv Recycl* 118:13–26. <https://doi.org/10.1016/j.resconrec.2016.11.016>
 16. Lugo-Arias J, Villa-Parejo J, Escorcía G et al (2025) Life Cycle Assessment of Magnesium-Impregnated Biochar Production and its Application for Nutrient Removal and Soil Improvement in Rice Cultivation. *Adv Sustain Syst* 9. <https://doi.org/10.1002/adsu.202500326>
 17. Emenike EC, Adeleke JA, Iwuzor KO et al (2025) Application of Rice Husks-Based Biochar for Removal of Pollutants from Water and Wastewater. *Sep Purif Rev* 1–22. <https://doi.org/10.1080/15422119.2025.2559238>
 18. Rajandran P, Masngut N, Manas NHA et al (2025) Fixed-bed adsorption for industrial wastewater purification: An in-depth review. *Int J Environ Sci Technol* 22:3943–3964. <https://doi.org/10.1007/s13762-024-06034-4>
 19. Kumar R, Rahman A, Lamba J et al (2025) Harnessing biochar for nitrate removal from contaminated soil and water environments: Economic implications, practical feasibility, and future perspectives. *Biochar* 7:94. <https://doi.org/10.1007/s42773-025-00486-8>
 20. El-Shafie AS, Rahman E, Gadelhak Y et al (2024) Techno-economic assessment of waste mandarin biochar as a green adsorbent for binary dye wastewater effluents of methylene blue and basic fuchsin: Lab- and large-scale investigations. *Spectrochim Acta Mol Biomol Spectrosc* 306:123621. <https://doi.org/10.1016/j.saa.2023.123621>
 21. Tran DT, Pham TD, Dang VC et al (2022) A facile technique to prepare MgO-biochar nanocomposites for cationic and anionic nutrient removal. *J Water Process Eng* 47:102702. <https://doi.org/10.1016/j.jwpe.2022.102702>
 22. Zhang M, Gao B, Yao Y et al (2012) Synthesis of porous MgO-biochar nanocomposites for removal of phosphate and nitrate from aqueous solutions. *Chem Eng J* 210:26–32. <https://doi.org/10.1016/j.cej.2012.08.052>
 23. Şentürk İ, Yıldız MR (2020) Highly efficient removal from aqueous solution by adsorption of Maxilon Red GRL dye using activated pine sawdust. *Korean J Chem Eng* 37:985–999. <https://doi.org/10.1007/s11814-020-0526-1>
 24. Nordine N, El Bahri Z, Sehil H et al (2016) Lead removal kinetics from synthetic effluents using Algerian pine, beech and fir sawdust's: optimization and adsorption mechanism. *Appl Water Sci* 6:349–358. <https://doi.org/10.1007/s13201-014-0233-3>
 25. Zhang S, Wang C (2023) Precise Analysis of Nanoparticle Size Distribution in TEM Image. *Methods Protoc* 6:63. <https://doi.org/10.3390/mps6040063>
 26. Xu X, Gao BY, Tan X et al (2011) Characteristics of amine-cross-linked wheat straw and its adsorption mechanisms for phosphate and chromium (VI) removal from aqueous solution. *Carbohydr Polym* 84:1054–1060. <https://doi.org/10.1016/j.carbpol.2010.12.069>
 27. Pimentel CH, Freire MS, Gómez-Díaz D, González-Álvarez J (2024) Continuous Adsorption of Acid Wood Dyes onto an Activated Carbon Prepared from Pine Sawdust. *Appl Sci* 14:841. <https://doi.org/10.3390/app14020841>
 28. Golie WM, Upadhyayula S (2016) Continuous fixed-bed column study for the removal of nitrate from water using chitosan/alumina composite. *J Water Process Eng* 12:58–65. <https://doi.org/10.1016/j.jwpe.2016.06.007>
 29. Thomas HC (1944) Heterogeneous Ion Exchange in a Flowing System. *J Am Chem Soc* 66:1664–1666. <https://doi.org/10.1021/ja01238a017>
 30. Song J, Zou W, Bian Y et al (2011) Adsorption characteristics of methylene blue by peanut husk in batch and column modes. *Desalination* 265:119–125. <https://doi.org/10.1016/j.desal.2010.07.041>
 31. Hu Q, Xie Y, Zhang Z (2020) Modification of breakthrough models in a continuous-flow fixed-bed column: Mathematical characteristics of breakthrough curves and rate profiles. *Sep Purif Technol* 238:116399. <https://doi.org/10.1016/j.seppur.2019.116399>
 32. Yoon YH, Nelson JH (1984) Application of Gas Adsorption Kinetics I. A Theoretical Model for Respirator Cartridge Service Life. *Am Ind Hyg Assoc J* 45:509–516. <https://doi.org/10.1080/15298668491400197>
 33. Han R, Wang Y, Zhao X et al (2009) Adsorption of methylene blue by phoenix tree leaf powder in a fixed-bed column: experiments and prediction of breakthrough curves. *Desalination* 245:284–297. <https://doi.org/10.1016/j.desal.2008.07.013>
 34. Clark RM (1987) Modeling TOC Removal by GAC: The General Logistic Function. *J AWWA* 79:33–37. <https://doi.org/10.1002/j.1551-8833.1987.tb02780.x>

35. Daffalla SB, Mukhtar H, Shaharun MS (2010) Characterization of Adsorbent Developed from Rice Husk: Effect of Surface Functional Group on Phenol Adsorption. *J Appl Sci* 10:1060–1067. <https://doi.org/10.3923/jas.2010.1060.1067>
36. Sooksawat N, Santibenchakul S, Kruatrachue M, Inthorn D (2021) Recycling rice husk for removal of phosphate and nitrate from synthetic and swine wastewater: Adsorption study and nutrient analysis of modified rice husk. *J Environ Sci Health Part A* 56:1080–1092. <https://doi.org/10.1080/10934529.2021.1962165>
37. Chen B, Chen Z, Lv S (2011) A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresour Technol* 102:716–723. <https://doi.org/10.1016/j.biortech.2010.08.067>
38. Hamzah S, Razali NA, Yatim NI et al (2018) Characterisation and performance of thermally treated rice husk as efficient adsorbent for phosphate removal. *J Water Supply: Res Technol - AQUA* 67:766–778. <https://doi.org/10.2166/aqua.2018.087>
39. Sarangi M, Bhattacharyya S, Behera RC (2009) Effect of temperature on morphology and phase transformations of nano-crystalline silica obtained from rice husk. *Phase Transitions* 82:377–386. <https://doi.org/10.1080/01411590902978502>
40. Zhu L, Lei H, Wang L et al (2015) Biochar of corn stover: Microwave-assisted pyrolysis condition induced changes in surface functional groups and characteristics. *J Anal Appl Pyrol* 115:149–156. <https://doi.org/10.1016/j.jaap.2015.07.012>
41. Jiang YH, Li AY, Deng H et al (2019) Characteristics of nitrogen and phosphorus adsorption by Mg-loaded biochar from different feedstocks. *Bioresour Technol* 276:183–189. <https://doi.org/10.1016/j.biortech.2018.12.079>
42. Gizaw A, Zewge F, Chebude Y et al (2022) Simultaneous nitrate and phosphate abatement using calcium silicate hydrate adsorbent: Fixed bed column adsorption study. *Surf Interfaces* 30:101961. <https://doi.org/10.1016/j.surf.2022.101961>
43. Najmi S, Hatamipour MS, Sadeh P et al (2020) Activated carbon produced from Glycyrrhiza glabra residue for the adsorption of nitrate and phosphate: batch and fixed-bed column studies. *SN Appl Sci* 2:773. <https://doi.org/10.1007/s42452-020-2585-7>
44. Manjunath SV, Kumar M (2021) Simultaneous removal of antibiotic and nutrients via Prosopis juliflora activated carbon column: Performance evaluation, effect of operational parameters and breakthrough modeling. *Chemosphere* 262:127820. <https://doi.org/10.1016/j.chemosphere.2020.127820>
45. Mekonnen DT, Alemayehu E, Lennartz B (2021) Fixed-Bed Column Technique for the Removal of Phosphate from Water Using Leftover Coal. *Materials* 14:5466. <https://doi.org/10.3390/ma14195466>
46. Mittal A, Singh R, Chakma S et al (2021) An integrated permeable reactive barrier and photobioreactor approach for simultaneous removal of nitrate, phosphate and hexavalent chromium: A combined batch and continuous flow study. *Bioresour Technol* 333:125201. <https://doi.org/10.1016/j.biortech.2021.125201>
47. Kwapinski W, Winterberg M, Tsotsas E, Mewes D (2004) Modeling of the Wall Effect in Packed Bed Adsorption. *Chem Eng Technol* 27:1179–1186. <https://doi.org/10.1002/ceat.200407001>
48. Olgun A, Atar N, Wang S (2013) Batch and column studies of phosphate and nitrate adsorption on waste solids containing boron impurity. *Chem Eng J* 222:108–119. <https://doi.org/10.1016/j.cej.2013.02.029>
49. Liu L, Ji M, Wang F (2018) Adsorption of Nitrate onto ZnCl₂-Modified Coconut Granular Activated Carbon: Kinetics, Characteristics, and Adsorption Dynamics. *Adv Mater Sci Eng* 2018. <https://doi.org/10.1155/2018/1939032>
50. Allahkarami E, Azadmehr A, Noroozi F et al (2022) Nitrate adsorption onto surface-modified red mud in batch and fixed-bed column systems: equilibrium, kinetic, and thermodynamic studies. *Environ Sci Pollut Res* 29:48438–48452. <https://doi.org/10.1007/s11356-022-19311-x>
51. Nguyen TAH, Ngo HH, Guo WS et al (2015) Adsorption of phosphate from aqueous solutions and sewage using zirconium loaded okara (ZLO): Fixed-bed column study. *Sci Total Environ* 523:40–49. <https://doi.org/10.1016/j.scitotenv.2015.03.126>
52. Ren Z, Xu X, Wang X et al (2016) FTIR, Raman, and XPS analysis during phosphate, nitrate and Cr(VI) removal by amine cross-linking biosorbent. *J Colloid Interface Sci* 468:313–323. <https://doi.org/10.1016/j.jcis.2016.01.079>
53. Ramirez A, Giraldo S, Garcia-Nunez J et al (2018) Phosphate removal from water using a hybrid material in a fixed-bed column. *J Water Process Eng* 26:131–137. <https://doi.org/10.1016/j.jwpe.2018.10.008>
54. Stepova K, Fediv I, Mažeikienė A et al (2023) Adsorption of Ammonium Ions and Phosphates on Natural and Modified Clinoptilolite: Isotherm and Breakthrough Curve Measurements. *Water (Basel)* 15:1933. <https://doi.org/10.3390/w15101933>
55. Ye Y, Wei Y, Gu Y et al (2020) Simultaneous removal of fluoride and phosphate in a continuous fixed-bed column filled with magnesite-pullulan composite. *J Alloys Compd* 838:155528. <https://doi.org/10.1016/j.jallcom.2020.155528>
56. Husein DZ, Al-Radadi T, Danish EY (2017) Adsorption of Phosphate Using Alginate-/Zirconium-Grafted Newspaper Pellets: Fixed-Bed Column Study and Application. *Arab J Sci Eng* 42:1399–1412. <https://doi.org/10.1007/s13369-016-2250-z>
57. He Y, Lin H, Dong Y et al (2016) Simultaneous removal of phosphate and ammonium using salt-thermal-activated and lanthanum-doped zeolite: fixed-bed column and mechanism study. *Desalin Water Treat* 57:27279–27293. <https://doi.org/10.1080/19443994.2016.1166459>
58. Gouran-Orimi R, Mirzayi B, Nematollahzadeh A, Tardast A (2018) Competitive adsorption of nitrate in fixed-bed column packed with bio-inspired polydopamine coated zeolite. *J Environ Chem Eng* 6:2232–2240. <https://doi.org/10.1016/j.jece.2018.01.049>
59. Rout PR, Bhunia P, Dash RR (2017) Evaluation of kinetic and statistical models for predicting breakthrough curves of phosphate removal using dolomite-packed columns. *J Water Process Eng* 17:168–180. <https://doi.org/10.1016/j.jwpe.2017.04.003>
60. Wang T, Zhang D, Fang K et al (2021) Enhanced nitrate removal by physical activation and Mg/Al layered double hydroxide modified biochar derived from wood waste: Adsorption characteristics and mechanisms. *J Environ Chem Eng* 9:105184. <https://doi.org/10.1016/j.jece.2021.105184>
61. Jellali S, Hadroug S, Al-Wardy M et al (2024) Phosphorus recovery from aqueous solutions by a Mg/Al-modified biochar from date palm wastes in column mode: adsorption characteristics and scale-up design parameters assessment. *Biomass Convers Biorefin* 15:27437–27452. <https://doi.org/10.1007/s13399-024-06435-y>
62. Zhang J, Huang W, Yang D et al (2022) Removal and recovery of phosphorus from secondary effluent using layered double hydroxide-biochar composites. *Sci Total Environ* 844:156802. <https://doi.org/10.1016/j.scitotenv.2022.156802>
63. Esmati F, Holliday MC, Zein SH et al (2024) Enhancing hexavalent chromium removal from textile effluent with low-cost adsorbent: simulation and a techno-economic study. *Int J Environ Sci Technol* 22:6345–6364. <https://doi.org/10.1007/s13762-024-05958-1>
64. García-Sánchez JJ, Solache-Ríos M, Alarcón-Herrera MT, Martínez-Miranda V (2016) Removal of fluoride from well water by modified iron oxides in a column system. *Desalin Water Treat* 57:2125–2133. <https://doi.org/10.1080/19443994.2014.980332>

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