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Utilizing Calcined Hard Clam Shells for Phosphate Removal using an Up-flow Column Reactor through Water Solution

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Abstract

Phosphate pollution in aquatic environments is a critical environmental issue that poses a significant threat to water quality and the ecosystem, primarily from agricultural runoff, industrial discharges, and domestic wastewater effluents. This research aims to evaluate the effectiveness of calcining hard clam shells in phosphate removal and to understand the mass transfer process within an up-flow column reactor. Experimental data was analyzed using an up-flow column reactor to study the adsorption of phosphate deposited on the surface of calcined hard clam shells. According to preliminary findings, calcined hard clam shells show great potential for use as phosphate adsorbents due to their promising capacity and efficiency. The primary materials responsible for phosphate removal are calcium oxide (CaO) and calcium carbonate ($CaCO_3$) generated through the calcination process, facilitating phosphate adsorption and precipitation. The analysis indicates that deeper adsorbent layers sustain better removal efficiencies throughout time. In contrast, shallower adsorbent layers approach solute saturation quickly through an up-flow column reactor. More extended periods of effective adsorption are provided by deeper adsorbent beds, according to the Bed Depth Service Time (BDST) model. These results are corroborated by the Thomas and Modified Mass Transfer Factor (MMTF) models, which demonstrate that while adsorption rates are higher in shallower beds, deeper beds have higher total capacities and longer service durations. This study contributes a thorough assessment of calcine hard clam shells as an affordable and environmentally friendly way to remove phosphate from wastewater, helping to reduce eutrophication in aquatic environments and improving tertiary wastewater treatment methods.

1. Introduction

Aquatic phosphate contamination is a serious environmental issue that risks ecosystem health and water quality [1]. Water bodies can become nutrient-rich due to phosphate inputs, mainly from industrial discharges, domestic wastewater effluents, and agricultural runoff [2]. Excessive algal blooms caused by eutrophication lower dissolved oxygen levels, disturb aquatic ecosystems, and reduce biodiversity. The adverse effects of eutrophication highlight the urgent need for efficient phosphate removal from wastewater before discharge into natural water bodies [3]. Phosphate levels in wastewater effluent pose a significant environmental challenge, yet monitoring and controlling them is often inadequate, particularly in developing countries like Malaysia.

In Malaysia, the regulation of phosphorus in domestic wastewater is primarily governed under the Environmental Quality Act 1974, particularly through the Environmental Quality (Sewage Effluents) Regulations 2009. These regulations set discharge standards based on sensitivity classifications, with stricter limits applied to environmentally sensitive areas. Specifically, the discharge standards for phosphorus are divided into Standard A and Standard B, depending on the sensitivity of the receiving water body. Standard A applies to environmentally sensitive areas, such as upstream water intake points, with a total phosphorus limit of 5.0 mg/L. Standard B, on the other hand, is applied to non-sensitive areas with a total phosphorus limit of 10 mg/L. However, Malaysia's effluent limits for phosphorus are generally higher compared to those in developed countries such as Canada and the United Kingdom, raising environmental concerns. For instance, Canada's limits vary by jurisdiction but are typically between 0.1 and 0.5 mg/L for sensitive areas, while the United Kingdom's limits for sensitive areas are generally below 0.5 mg/L [4]. International standards set by organizations such as the USEPA and EU also advocate for stricter phosphorus controls, highlighting the gap in Malaysia's regulations, which allows higher phosphorus discharge and increases the risk of environmental degradation

Several techniques have been applied for phosphate removal, including chemical precipitation, biological treatment, and adsorption using synthetic materials. While these methods are effective, they often involve high operational costs, complex handling, and potential secondary pollution. Adsorption, by contrast, offers a simpler, more economical, and effective solution, especially when using naturally abundant materials. Among various adsorbents, calcined hard clam shells stand out as a promising alternative due to their high calcium content, large specific surface area, low cost, and environmental sustainability. These properties make calcined clam shells an attractive option compared to conventional adsorbents like activated carbon or synthetic resins. Additionally, their reuse not only mitigates waste from the seafood industry but also provides a circular economy benefit by valorizing by-products. Previous studies have reported the use of various clamshells materials such as clamshell waste [21] and calcined mussel shells for phosphate adsorption, all demonstrating good removal efficiency due to the presence of reactive calcium compounds. Despite their potential, limited studies have explored the use of calcined hard clam shells for phosphate removal, making this study an important step toward evaluating their effectiveness and exploring the mass transfer processes involved. This study, therefore, evaluates the effectiveness of calcined hard clam shells as an adsorbent for phosphate removal and examines the mass transfer processes involved within a hydrodynamic up-flow column reactor. The findings aim to contribute to the development of sustainable, low-cost wastewater treatment technologies, providing an environmentally friendly solution to mitigate eutrophication and preserve aquatic ecosystems.

2. Material and Method

2.1 Preparation for Adsorbent

A multi-step modification procedure makes the calcined hard clam shells into the adsorbent for efficient adsorption functionality [5]. The hard clam shells were washed with tap water to remove dirt, debris, and organic materials from their surface. Next, they were cleaned with deionized water to eliminate any remaining contaminants, such as chemicals or salts. After washing, the surface is dried in the sun for five to six hours to eliminate surface moisture. They are placed in an oven for two days to dry the shells completely. Any residual moisture that could negatively impact subsequent processing steps is eliminated during the oven's drying period. Subsequently, the dried shells undergo a grinding process to reduce their size and increase their surface area, improving their adsorption availability. After that, it is sieved to produce uniformly sized particles in the range of 1.18-2.36cm, which is crucial for maintaining consistent adsorption efficiency. The most critical stage in this preparation procedure is calcination. After sieving, the particles undergo a two-hour heating procedure in a furnace at 900 °C, which alters some of their chemical and physical characteristics (loss of volatile materials, increased surface area, and pore formation) [6] [7]. These enhancements enhance the adsorbent's capacity to attract and hold adsorbates significantly. After cooling, the calcined material is weighed to determine the precise amount of adsorbent ready for dosing in subsequent applications in columns with different column heights: 1, 2, 3, 4, 6, and 8 cm, respectively.

2.2 Preparation for Aqueous Solution

Starting from a more concentrated stock solution, a series of dilution procedures are required to prepare an aqueous solution containing 10ppm (parts per million) of phosphate (PO_4). The procedure starts by computing the molecular weight of the chemical containing phosphate to ascertain the precise mass necessary to make the first solution. This calculation is essential because it guarantees that the right amount of the compound is used to reach the required concentration in the solution. To start, a 1L of 100ppm PO_4^{3-} is manufactured by combining 0.1433g of potassium dihydrogen phosphate, KH_2PO_4, with 1L of deionized water. This process creates a stock of 100ppm solution of PO_4^{3-}. This stock solution was then diluted to different concentrations of 50 ppm and 10 ppm PO_4^{3-}. The dilution process of 50ppm PO_4^{3-} was done by adding 500ml of 100ppm solution into a 1L volumetric flask. 500ml of deionized water was added to the flask to create a stock solution of 50ppm PO_4^{3-}.

Lastly, to produce 10ppm PO_4^{3-} solution, 200ml of 50ppm PO_4^{3-} solution was added into 1L of volumetric flask, and deionized water was topped up to 1L. This process was repeated to produce a stock solution of 10ppm PO_4^{3-}.

2.3 Column Studies

Column studies using an up-flow column reactor are essential for evaluating the adsorption performance of different adsorbent bed heights in removing contaminants from aqueous solutions. In these studies, a systematic approach is employed to assess the effectiveness of the adsorbent material in capturing and eliminating phosphate ions (PO_4^{3-}) from a synthetic solution. The setup consists of a tank, a peristaltic pump, and a series of up-flow columns filled with varying amounts of adsorbent material, as shown in Fig. 1.

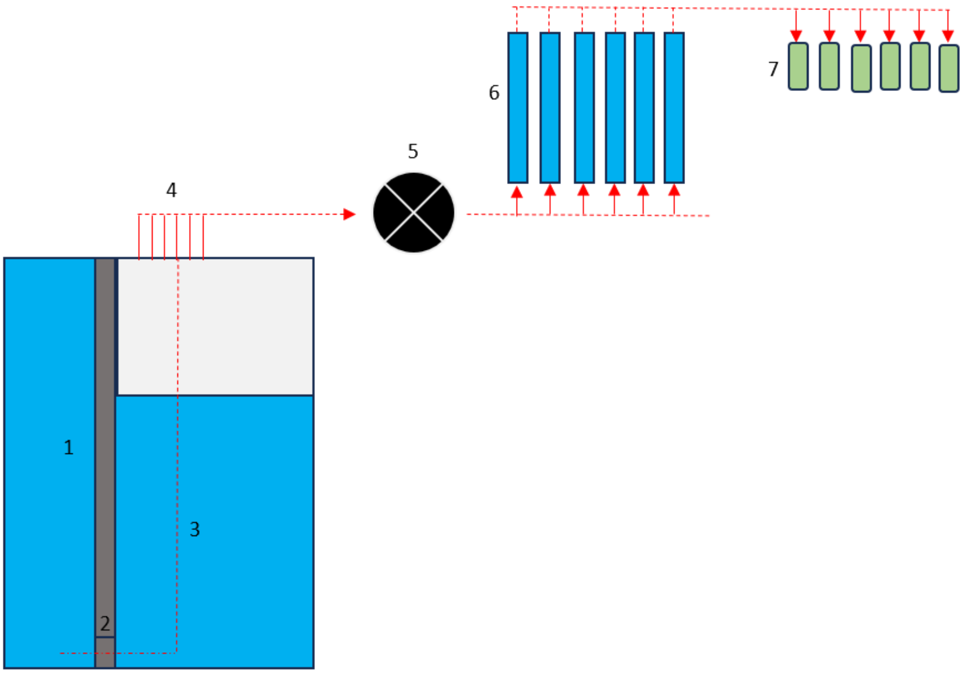


Fig. 1 *Schematic of the Up-flow column reactor system used in this study with (1) storing tank; (2) perforated acrylic feet with a hole diameter of 2 mm; (3) aqueous solution collection station; (4) silicone tube; (5) peristaltic pump; (6) up-flow column packed with calcined hard clam shell adsorbent; and (7) sampling beaker*

The process begins by filling a tank with an aqueous solution containing 10 ppm of phosphate (PO_4^{3-}), which serves as the effluent for the experiment. This tank is the source of effluent pumped into the column reactor system. The effluent transfer from the tank to the columns is controlled using a peristaltic pump, which ensures a consistent flow rate (Q) ranging from 2 to 100 mL/min [8]. The pump's flow rate can be adjusted depending on the study's requirements, allowing for the simulation of different hydraulic conditions and contact times between the effluent and the adsorbent, as shown in Table 1.

Table 1 *Dimensions and operational parameters of the Up-flow column reactor treatment system, including hydraulic retention time, flow rate, column height, internal diameter, material type, bed heights, adsorbent mass, and particle size range*

Parameter	Unit	Dimension
Hydraulic retention	h	0.584
Flow rate	L h^{-1}	0.1933
Column height	cm	23
Internal diameter	cm	2.5
Column material	-	Acrylic
Bed height	cm	1;2;3;4;6;8
Amount of Calcined Hard Clam Shell in bed	g	4.74; 7.31; 10.22; 13.92; 20.78; 29.50
Particle size range	mm	1.18 to 2.36

The six up-flow columns that comprise the column studies are filled with adsorbent material at varying bed heights: 1 cm, 2 cm, 3 cm, 4 cm, 6 cm, and 8 cm. To maximize the time that the phosphate ions in the solution and the adsorbent material are in touch, the effluent is injected into the bottom of each column and flows upward through the adsorbent bed. The up-flow design guarantees efficient use of the full adsorbent bed by preventing channeling. The ability to assess the effects of varied adsorbent concentrations on removal capacity and efficiency is made possible by the different bed heights, which aids in determining the ideal column conditions for phosphate removal.

Samples are taken from the outputs for analysis once the effluent has passed through the columns. The amount of phosphate left in the solution following treatment is ascertained by analyzing the data from these samples, which offers information on the effectiveness of each column configuration's adsorption process. The outcomes of these column studies are essential for comprehending the dynamics of the adsorption process in continuous flow scenarios and offer helpful information for expanding the procedure for larger-scale water treatment applications. The performance of the Up-flow Column Reactor was analyzed based on the concentrations of PO_4^{3-} monitored at the inlet and outlet of the Up-flow Column Reactor treatment system during the experimental period of 66 days. The PO_4^{3-} measurements were determined by the amino acid method, and the PO_4^{3-} analysis was achieved using DR6000.

2.4 Modelling Data Analysis

2.4.1 Removal Efficiency

The effectiveness of the Up-flow Column Reactor in eliminating the pollutants of PO_4^{3-} was utilised to evaluate the adsorption capacity of calcined hard clam shell, which was employed as an adsorbent. The Up-flow Column Reactor's performance may be computed using the following formula based on data from monitoring the PO_4^{3-} concentrations at the treatment system's input and outlet as equation (1).

$$E = \frac{C_i - C_f}{C_i} x\ 100\% \quad (1)$$

where E is the efficiency of the Up-flow Column Reactor to remove PO_4^{3-} from aqueous solution (%), C_i is the concentration of either PO_4^{3-} at the inlet of the Up-flow Column Reactor treatment system (mg/L), and C_f is the concentration of either PO_4^{3-} at the outlet of the Up-flow Column Reactor treatment system (mg/L) [9].

2.4.2 Bed Depth Service Time Models

The Bed Depth Service Time (BDST) model is an essential mathematical model used in adsorption column studies to predict the performance and efficiency of fixed-bed adsorbent systems in removing contaminants from fluid streams. The BDST model focuses explicitly on the relationship between the depth of the adsorbent bed in a column and the time required for the column to reach a specific breakthrough concentration. The BDST model assumes a linear relationship between the bed depth (Z) and the service time (t) for a given contaminant concentration and flow rate [10]. The equation provides this relationship as equation (2).

$$t = (a\ x\ h) - b \quad (2)$$

$$b = \left(\frac{1}{K_a} x\ C_o\right) ln - b \quad (2)$$

$$b = \left(\frac{1}{K_a} x\, C_o\right) ln\left(\frac{C_o}{C_s} - 1\right) \tag{3}$$

$$c = \frac{N_o}{C_o\, x\, v} \tag{4}$$

$$K_a = \left(\frac{1}{b} x\, C_o\right) ln\left(\frac{C_o}{C_s} - 1\right) \tag{5}$$

Where equations (3) and (4) are constants (in h/cm). The value of No for a given set of Co and ν values can be determined by plotting time with the height of the column, which yields a linear function graph with an as the slope and b as the Y-intercept. Equation (5) can determine the variant Ka based on the percentage of PO_4^{3-} a breakthrough. The retention coefficient depends on the velocity of the PO_4^{3-} passing the up-flow column reactor (h/cm), and b is the contact time constant that depends on the availability of the space and acceptor sites of the Calcined Hard Clam Shell adsorbent [11] [12].

2.4.3 Thomas Model

The Thomas Model is a classical and widely used mathematical model in adsorption science that describes the behavior of fixed-bed adsorption columns. It is specifically designed to predict the performance of these columns in removing contaminants from a fluid stream. The Thomas Model is particularly effective for systems where adsorption follows a linear isotherm, meaning the amount of adsorbate adsorbed is directly proportional to its concentration in the fluid. A simplification of the equation can be written in the linear equation (6).

$$ln\left(\frac{C_o}{C_s} - 1\right) = -(c\, x\, t) + d \tag{6}$$

$$d = \frac{K_T\, x\, q_o\, x\, m}{Q} \tag{7}$$

$$c = K_T\, x\, C_o \tag{8}$$

with equation (7) as the Y-intercept is a constant since the experiment was set at a constant flow rate, equation (8) as the slope is a constant (/h), and t = V/Q as the service time (h). If the values of c as the slope and d as the Y-intercept have been confirmed from the linear graph of ln(Co/Cs—1) versus t, then the values of K_T and q_o can be computed for a given flow rate.

2.4.4 Modified Mass Transfer Model

Modified Mass Transfer Models (MMTF) are advanced mathematical models used to describe and predict the kinetics of adsorption processes in fixed-bed columns. These models are developed to provide a more accurate understanding of the mass transfer mechanisms that govern the adsorption of contaminants onto adsorbent materials under dynamic flow conditions. MMTF models consider various factors such as adsorption kinetics, external film diffusion, intraparticle diffusion, and the adsorbent's capacity to capture contaminants. The simplification of equation yielding a linear equation can be mathematically as equation (9).

$$\ln(q) = \frac{1}{\beta} x \ln(t) + B \tag{9}$$

where B is the potential mass transfer index relating to driving force of PO_4^{3-} mass transfer from bulk water to acceptor sites (mg/g).

$$B = \frac{\ln([k_L a]_g) - ln\left\{ln\left(\frac{C_o}{C_s}\right)\right\}}{\beta} \tag{10}$$

$$[k_L a]_g = \frac{ln\left(\frac{C_o}{C_s}\right)}{e^{-\beta q}\ x\ t} \tag{11}$$

$$[k_L a]_f = [k_L a]_g\ x\ e^{-\beta q} \tag{12}$$

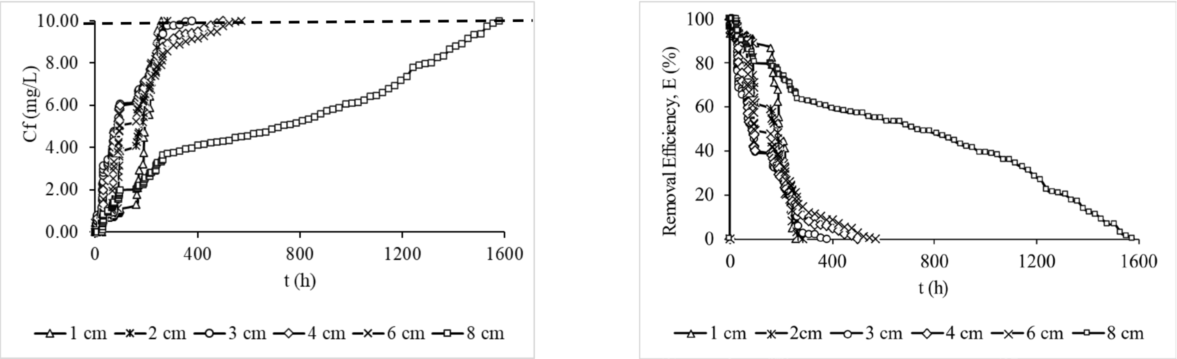
$$[k_L a]_d = [k_L a]_g - [k_L a]_f \tag{13}$$

A correlation of the global, external, internal mass transfer factor can be written in the equation (11), (12) and (13) where $[kLa]_f$ is the external mass transfer factor or film mass transfer factor (/h) while $[kLa]_d$ is the internal mass transfer factor or porous difusion factor (/h) [13].

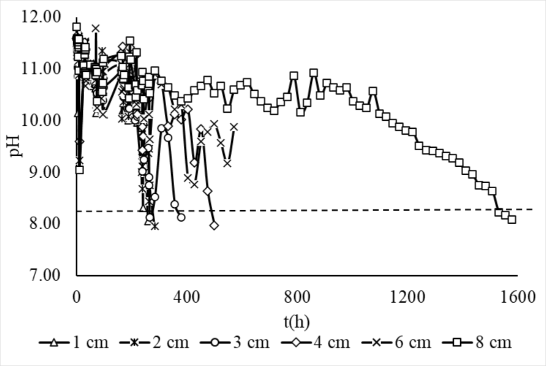
3. Results and Discussion

3.1 Performance of Up-flow Column Reactor Under Operating Conditions

This study investigates mass transfer processes in a hydrodynamic column arrangement, comprehends adsorption mechanisms, and assesses the effectiveness of calcining hard clam shells. The results are intended to aid in creating environmentally friendly wastewater treatment plans that reduce phosphate pollution and safeguard aquatic environments. Fig. 2 (a) shows C_f at six (1 cm, 2 cm, 3 cm, 4 cm, 6 cm, and 8 cm) levels, demonstrating the variations in time-dependent behavior at different levels, i.e., adsorption dynamics over time. The C_f values indicate a significant enhancement of leaching losses for the shallow depths, with 1 cm, 2 cm, and 3 cm showing a sharp increase in concentration up to around 400 hours, corresponding to a higher velocity of solute reaching and saturation at these locations. Phosphate loadings at lateral positions from 1 cm to 6 cm increase sharply, but concentrations remain constant at 8 cm, indicating that lateral solute migration is less of a concern as the depth of the medium increases.



(a) **(b)**



(c)

Fig. 2 *Performance of the Up-flow column reactor under varying adsorbent bed heights: (a) Final concentration (Cf) for phosphate (PO43-) (mg/L) versus time, (t) (h); (b) The removal efficiency (E%) against time for each adsorbent height (h); (c) pH variation of effluent across different bed heights during the experimental period*

These highest concentrations, approached by about 800 hours but in some cases not achieved until after 1000 hours, reach nearly 10 mg/L for the first depth of only 1 cm and rise more slowly and even later for depths further down as shown in Fig. 2(a). This indicated that the solute transport was depth-dependent, with the shallow adsorbent layers reaching saturation first due to higher solute exposure. At the same time, deeper labor beds exhibited some retardation in the adsorption and dilution of the time, as reflected by a continual rise in C_f values at later times. The slower breakthrough at greater depths emphasizes the system's effective retention for long periods under such conditions.

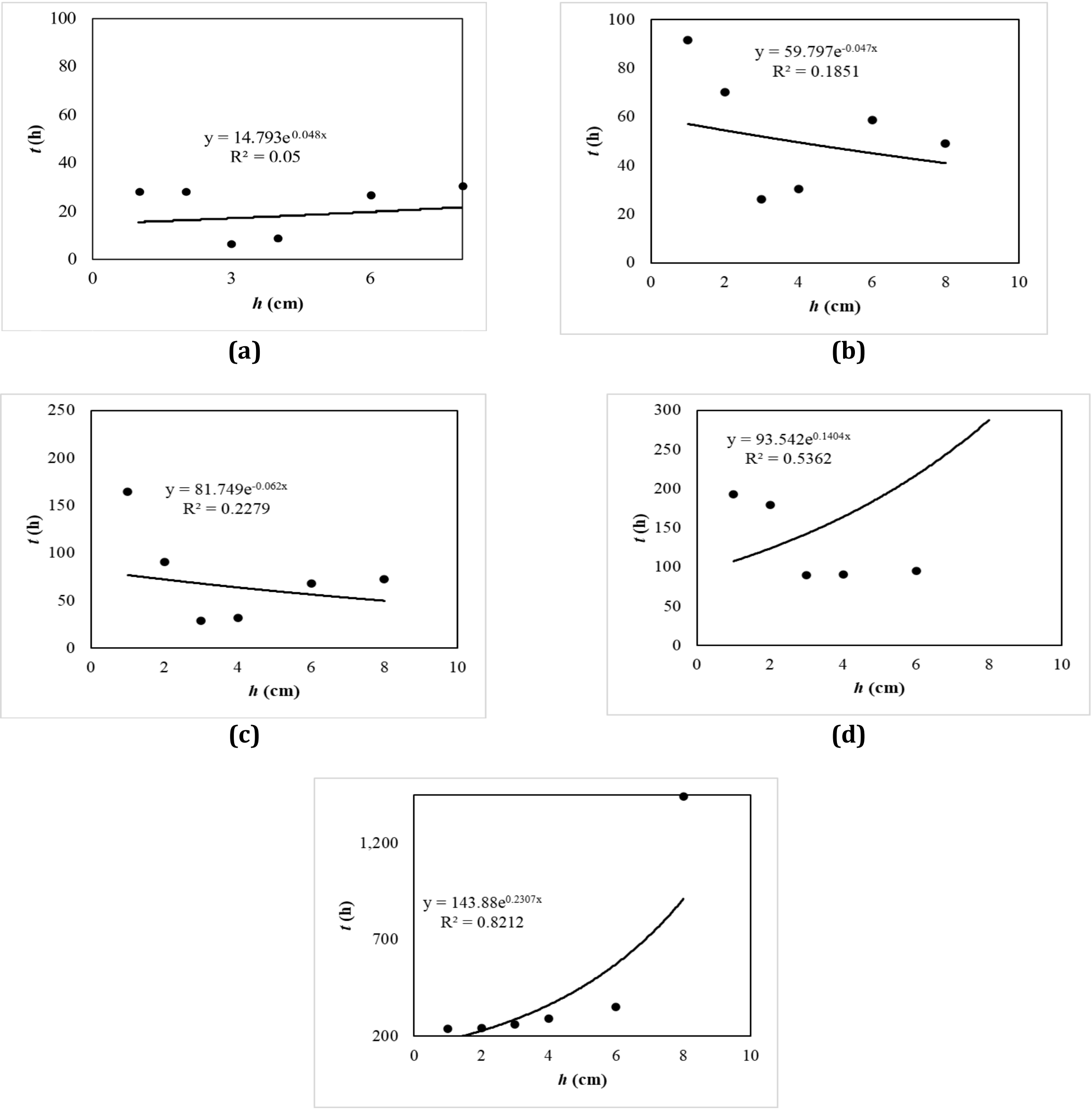
The adsorption efficiency, observed with different filter thicknesses of 1 cm, 2 cm, 3 cm, 4 cm, 6 cm, and 8 cm over time, was aimed at understanding the long-term performance of the adsorption system during the experiment. Initially, each had a very high removal efficiency, E, ranging from 60% to 100% for the first few hours, as depicted in Figure 2 (b). In thinner layers (1 cm to 6 cm), after some time had elapsed, especially in the first 400 hours of operation, it showed a rapid decline to near-zero efficiency. While the 8-cm thickness of the filter media maintained higher removal efficiencies beyond 400 hours and managed a slower decline compared to thinner layers, it continued to operate at a removal efficiency above 40% until approximately 1600 hours. This qualitatively informs that thicker adsorbent media could be better at providing long-term performance, hence their potential for use in long-term applications to maintain higher removal efficiencies over extended periods of operational time. Probably, the efficiency degraded gradually due to a gradual development of clogging or saturation of the adsorbent with particles, reducing its adsorption capacity.

These pH changes, monitored through the height of adsorbent of 1 cm, 2 cm, 3 cm, 4 cm, 6 cm, and 8 cm, were plotted against time for a better system performance study during experimentation. Initially, the pH values were within the range of approximately 9.0 to 11.5 for all adsorbent dosages, showing the alkaline condition at the commencement of the experiment, as portrayed by Figure 2 (c). The first points of pH recorded during the first 400 hours for thinner layers, ranging from 1 cm up to 6 cm, were highly fluctuating. In most cases, a rapid decline was found in the 3 cm and 4 cm layers; their pH values suddenly plunged to less than 9.0. Meanwhile, other thicknesses 8 cm layer showed more discreet variations: many points of the pH remained above 10.0 for some time and afterward decreased gradually to about 9.0 beyond 1000 h. This stability can be explained by the hypothesis that thicker filter media buffer rapid pH changes that may be induced by material accumulation and biochemical reactions within the filter. After 800 hours, the pH values across all layers declined, but at much-reduced rates, among which the 8-cm layer was the slowest. This gradual decrease could be explained by continuous biological processes, such as aerobic digestion, which would produce acid metabolites, reflecting their action in reducing pH over the period [14]. Higher pH values obtained in the thicker layers, for example, 8, indicate better performance in maintaining an alkaline environment within this layer, which is essential for several treatment processes [15].

3.2 Analysis of Bed Depth Service Time Model

The Bed Depth Service Time (BDST) model is an essential mathematical model used in adsorption column studies to predict the performance and efficiency of fixed-bed adsorbent systems in removing contaminants from fluid streams. The BDST model focuses explicitly on the relationship between the depth of the adsorbent bed in a column and the time required for the column to reach a specific breakthrough concentration. Breakthrough occurs when the contaminant concentration in the effluent (the treated fluid leaving the column) reaches a predetermined level, indicating that the adsorbent bed is becoming saturated and its removal efficiency is declining. The BDST model helps optimize the design and operation of fixed-bed adsorption systems by providing a means to estimate the necessary bed depth and service time for desired treatment outcomes. The linear relationship between bed depth and service time implies that increasing the bed depth will proportionally increase the service time before breakthrough occurs for a given contaminant concentration and flow rate [16]. This is because a deeper bed provides more adsorbent material, allowing more contaminants to be adsorbed before the adsorbent becomes saturated. Conversely, reducing the flow rate at a fixed bed depth will also increase the service time, as the contaminants will have more contact time with the adsorbent, enhancing adsorption efficiency [17].

The analysis of the BDST model's goodness of fit is illustrated in Figure 3, which presents the relationship between bed depth (h in cm) and breakthrough time (t in hours) for different breakthrough concentrations of solute (5%, 10%, 20%, 50%, and 90%). The data for each concentration are modeled using an exponential curve, and the quality of the fit is evaluated using the R^2 value, which quantifies the degree of correlation between the experimental data and the model.



(a) **(b)**

(c) **(d)**

(e)

Fig. 3 *BSDT model interpolation for phosphate adsorption at different breakthrough percentages: (a) 5%; (b) 10%; (c) 20%; (d) 50%; and (e) 90% breakthrough, showing the relationship between bed depth (h, cm) and service time (t, hours)*

Fig. 3 represents the BDST model interpolation for different solute concentrations, likely at 5%, 10%, 20%, 50%, and 90%, showing the relationship between bed depth (h in cm) and breakthrough time (t in hours). The equations and R^2 values indicate the trend and fit quality of the exponential model applied. In Fig. 3, the relationship shows a slightly positive trend with a very low R^2 value of 0.05, suggesting a poor correlation. The Fig. 3(b) and Fig. 3(c) display negative trends with increasing bed depth and slightly better fits (R^2 values of 0.1851 and 0.2279, respectively), though still indicating weak correlations. In Fig. 3(d) (50% breakthrough), the model equation $y = 93.542e^{0.1404x}$ with an R^2 value of 0.5362 indicates a moderate data fit to the exponential curve. The fifth graph (90% breakthrough) presents a more pronounced curve, represented by the equation $y = 143.88e^{0.2307x}$ with a higher R^2 of 0.8212, suggesting a better correlation between the model and experimental data. The higher R^2 for the 90% breakthrough indicates that the model accurately predicts service times for higher pollutant concentrations. Both suggest an exponential relationship between bed height and service time, with the 90% breakthrough showing a steeper curve due to higher contaminant load [18]. The trend across all figures suggests an exponential relationship between bed depth and service time, with a more significant correlation observed at higher breakthrough concentrations, particularly at the 90% level. The model is more accurate for higher contaminant loads, as indicated by the sharper curve and higher R^2 value.

Table 2 *Summary of Bed Depth Service Time (BDST) model parameters for phosphate adsorption onto calcined hard clam shells at different breakthrough concentrations (5%, 10%, 20%, 50%, and 90%), including adsorption rate constants, column service times, and model fit (R^2 values).*

C_s/C_o (%)	a (h cm^{-1})	b (dimensionless)	R^2	N_o (mg L^{-1})	K_a (L h^{-1} mg^{-1})
5	14.793	0.048	0.050	5824.544	6.134
10	59.797	-0.047	0.185	23544.260	-4.675
20	81.749	-0.062	0.228	32187.563	-2.236
50	93.542	0.140	0.536	36830.897	0.000
90	143.880	0.231	0.821	56650.804	-0.952

Table 2 summarizes the results of using BDST (Bed Depth Service Time) models for analyzing the adsorption of phosphate ions (PO_4^{3-}) onto calcined hard clam shells. Interpolation for different concentrations of a solute, likely at 5%, 10%, 20%, 50%, and 90%, showing the relationship between bed depth (h in cm) and breakthrough time (t in hours). Columns likely represent breakthrough time, adsorption rates, rate constants, and efficiency parameters like bed depth service times and capacities. The positive and negative values indicate variations in adsorption effectiveness, with optimal performance near 50, where values stabilize (e.g., zero relative error). High values at 90 suggest phosphate removal efficiency improves as time increases but fluctuates due to model parameters [19]. The table further shows that, for higher concentrations (50% and 90%), the adsorption rate constants (Ka) show a positive trend, indicating an increase in the rate of adsorption as the contaminant concentration rises. However, for lower concentrations (5%, 10%, and 20%), the rate constants are negative, which could be due to inconsistencies in the adsorption process or model fitting at these lower concentrations. In conclusion, while the BDST model demonstrates varying degrees of fit across different concentrations, the model performs better at higher breakthrough concentrations (50% and 90%), where the R^2 values indicate stronger correlations. The model's applicability for designing fixed-bed adsorption systems can be improved by focusing on these higher contaminant concentrations, where the relationship between bed depth and service time is more accurately predicted. The BDST model analysis revealed that higher bed depths significantly prolong the service time, with an R^2 value of 0.8212 at 90% breakthrough, indicating a good model fit and supporting the practical implementation of deeper columns for enhanced phosphate removal efficiency.

3.3 Analysis of Thomas Model

The Thomas Model is a classical and widely used mathematical model in adsorption science that describes the behavior of fixed-bed adsorption columns. It is specifically designed to predict the performance of these columns in removing contaminants from a fluid stream. The model is named after Thomas, who developed it in the 1940s to address the need for a theoretical framework to quantify fixed-bed systems' adsorption capacity and efficiency. The Thomas Model is particularly effective for systems where adsorption follows a linear isotherm, meaning the amount of adsorbate adsorbed is directly proportional to its concentration in the fluid. The core principle of the Thomas Model is to relate the concentration of the contaminant in the effluent (the treated fluid exiting the column) to the amount of adsorbate removed by the adsorbent over time. The model assumes that the adsorption process in the column is governed by a first-order reaction and that the adsorbent has a constant adsorption rate. The Thomas Model provides a formula that describes the breakthrough curve, the plot of contaminant concentration in the effluent versus time as the fluid passes through the column.

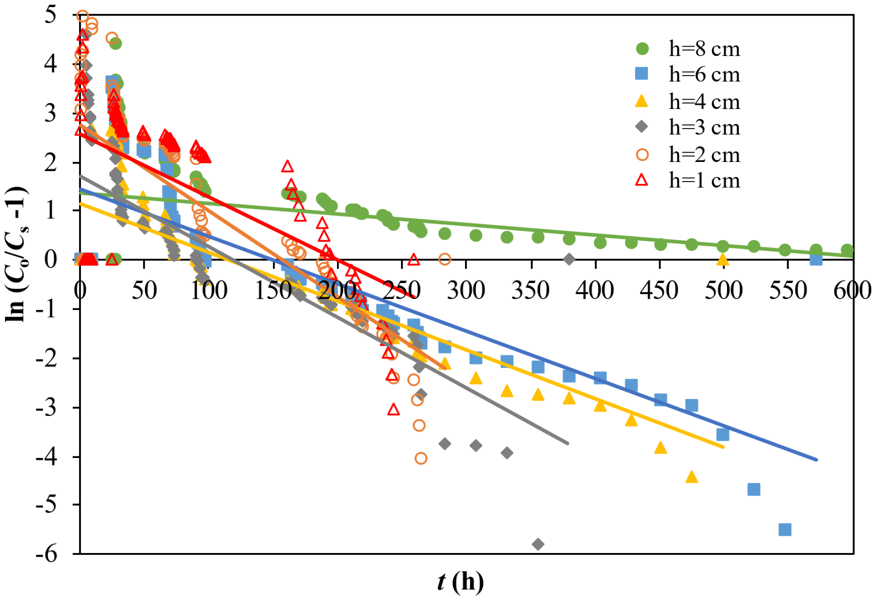


Fig. 4 *Linearized Thomas model plots: ln[(Co/Cs) – 1] versus service time (t, hours) for the adsorption of phosphate onto calcined hard clam shell packed beds at six different depths (2 cm, 2 cm, 3 cm, 4 cm, 6 cm and 8 cm)*

Fig. 4 depicts the adsorption of phosphate ions (PO_4^{3-}) at various bed depths (h). The six depths, which vary in size from 1 to 8 cm, are each indicated by unique lines and markings. The result suggests the adsorption process by showing a generally declining trend in the value of ln[(C_0/C_s) - 1] over time for all depths. The drop rate varies with bed depth: shallower beds (e.g., h = 1 cm) show a sharper decline, indicating faster saturation, whereas deeper beds (e.g., h = 8 cm) show a slower and more progressive reduction, suggesting a delayed breakthrough. The lines' adsorption kinetics are depicted by the slopes, where deeper beds retain adsorption capability for a more extended period, whereas shallower beds tend to exhaust more quickly. The patterns emphasize how crucial bed depth is for maximizing the effectiveness of phosphate removal over time.

Table 3 *Thomas model analysis for phosphate (PO43) adsorption onto calcined hard clam shells at different packed-bed heights (1 cm to 8 cm), showing kinetic constants, adsorption capacities, and model fitting (R^2 values)*

h (cm)	$k_T \times C_o$ (h^{-1})	$k_T \times q_o \times Q/m$ (dimensionless)	R^2	k_T ($L\ h^{-1}\ mg^{-1}$)	*m* (mg)	q_o ($mg\ g^{-1}$)
1	0.0127	2.5537	0.369	0.0013	4743.5	0.08
2	0.0176	2.7525	0.583	0.0018	7310.0	0.04
3	0.0144	1.7026	0.659	0.0014	10220.5	0.02
4	0.0099	1.1424	0.634	0.0010	13919.4	0.02
6	0.0122	1.5784	0.632	0.0012	20780.0	0.01
8	0.0022	1.3648	0.557	0.0002	29495.3	0.04

Table 3 presents the analysis of using Thomas models for the adsorption of phosphate ions (PO_4^{3-}) onto calcined hard clam shells across different bed depths (1, 2, 3, 4, 6, and 8 cm). The subsequent columns display various adsorption parameters, such as the adsorption rate constant, the Thomas constant, and breakthrough-related variables. As the bed depth increases, the Thomas constant and other values show noticeable variations, reflecting how the depth of the packed bed impacts the adsorption performance. For instance, deeper beds (like 8 cm) exhibit lower adsorption rate constants but greater total adsorption capacity, as evidenced by the more significant value in the last column, indicating that greater bed depths are more efficient at removing phosphate ions over longer durations. The decreasing values in adsorption rate with increasing bed depth suggest slower phosphate uptake at higher depths. In contrast, higher breakthrough times and capacities imply better long-term performance at greater depths. The Thomas Model analysis revealed that deeper bed depths result in slower adsorption kinetics and improved phosphate removal efficiency, as demonstrated by the lower adsorption rate constants at higher bed depths (0.0022 h^{-1} at 8 cm), but a greater overall adsorption capacity, indicated by higher total adsorption values (29495.3 mg). This suggests that while the adsorption rate decreases with increasing bed depth, the system is capable of maintaining higher phosphate removal efficiency over an extended period, making deeper beds more effective for long-term adsorption applications. A similar trend was observed where powdered clamshell adsorbent achieved higher nickel removal capacities at lower flow rates and greater bed depths, with the Thomas model fitting well to the experimental data ($R^2 > 0.98$) [21]. Although the current study showed moderate R^2 values (0.369 to 0.659), the observed relationship between bed depth and adsorption capacity aligns with the findings of [21] further validating the applicability of the Thomas model for evaluating phosphate and heavy metal removal in packed-bed systems.

3.4 Analysis of Modified Mass Transfer Factor Model

Modified Mass Transfer Models (MMTF) are advanced mathematical models used to describe and predict the kinetics of adsorption processes in fixed-bed columns. These models are developed to provide a more accurate understanding of the mass transfer mechanisms that govern the adsorption of contaminants onto adsorbent materials under dynamic flow conditions. MMTF models consider various factors such as adsorption kinetics, external film diffusion, intraparticle diffusion, and the adsorbent's capacity to capture contaminants. Unlike simpler models that often rely on assumptions like equilibrium or ideal conditions, MMTF models incorporate modifications that account for real-world complexities, such as non-linear adsorption isotherms, heterogeneous adsorbent properties, and varying flow dynamics. These modifications make MMTF models more suitable for predicting the performance of adsorption systems in practical applications.

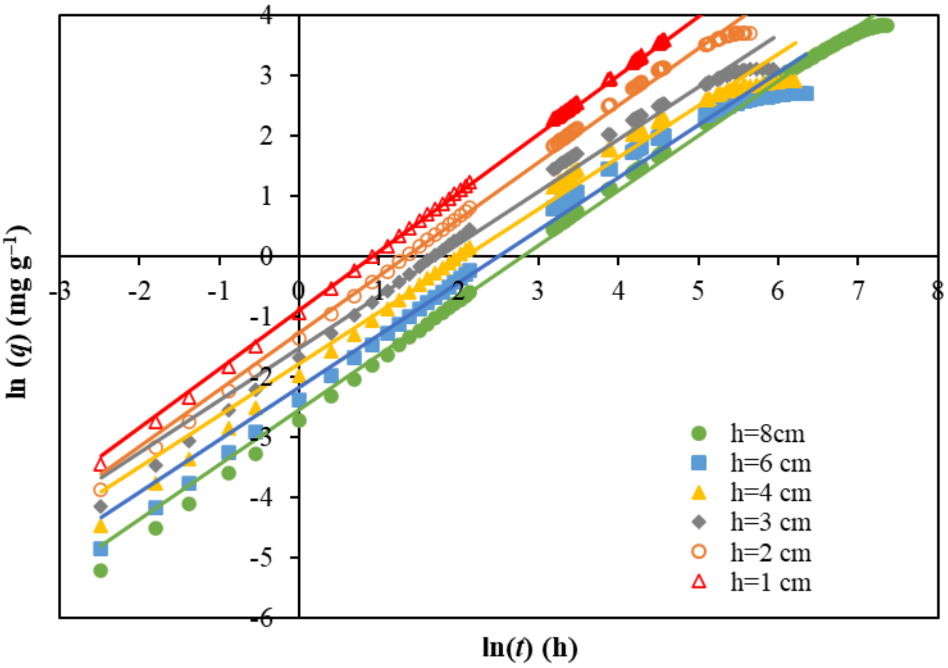


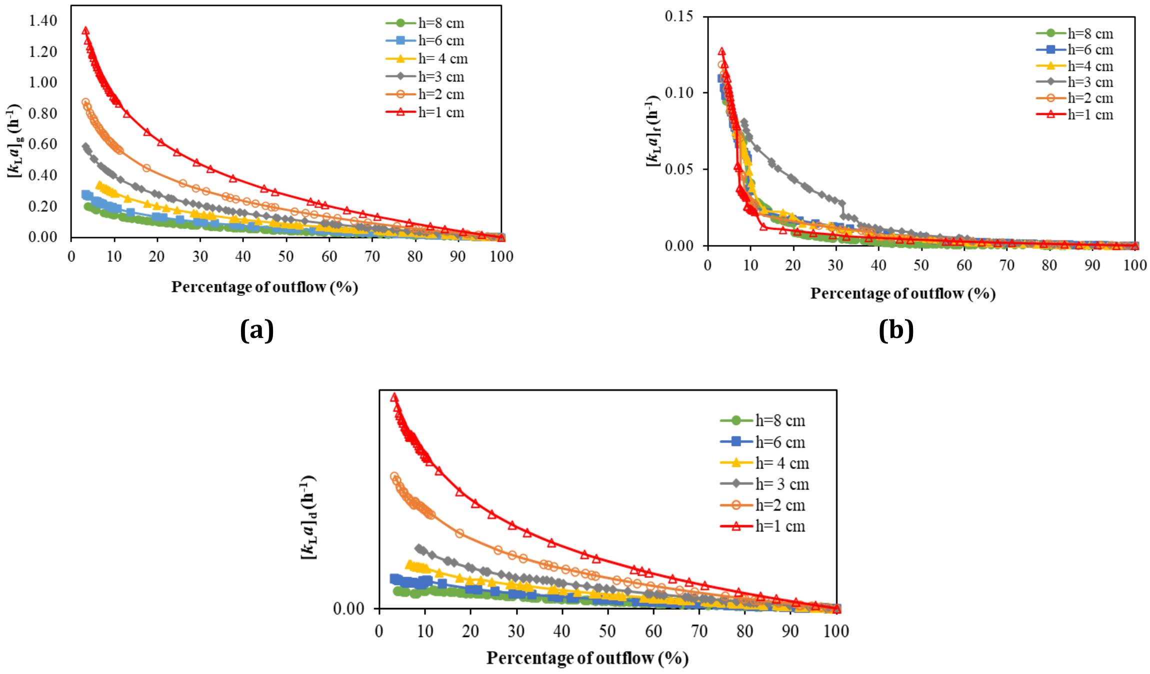
Fig. 5 *Linear regression analyses of the MMTF model: ln(q) versus ln(t) for the adsorption of phosphate onto Calcined Hard Clam Shell adsorbent at various packed-bed heights (1 cm to 8 cm)*

The results in Fig. 5 demonstrate that the adsorption of phosphate ions (PO_4^{3-}) onto calcined hard clamshell, analyzed using the MMTF (Modified Mass Transfer Factor) model, follows a linear relationship between ln(q) and ln(t). Each regression line represents the adsorption process at different adsorbent heights (h) ranging from 1 cm to 8 cm. The data show that as the height of the calcined clam shell increases, the slope of the regression lines decreases, indicating a faster adsorption rate for smaller adsorbent heights (h = 1 cm and 2 cm), shown by the steepest red and orange curves. In contrast, the adsorption capacity (q) increases with larger adsorbent heights, as indicated by the more elevated curves for h = 6 cm and h = 8 cm (blue and green). This suggests that while the adsorption rate is faster for smaller amounts of the adsorbent, larger amounts allow for greater total adsorption over time. The results are consistent with the expectations of the MMTF model, indicating that both time and adsorbent mass significantly affect the adsorption process.

Table 4 *Linear regression results of the Modified Mass Transfer Factor (MMTF) model for phosphate adsorption onto calcined hard clam shells at different packed-bed heights, presenting regression coefficients, mass transfer indices (B), and model fit (R^2 values)*

Equation	*h* (cm)	*b* (g h mg^{-1})	*B* (mg g^{-1})	R^2
y = 0.985x-0.919	1	1.015	-0.919	0.998
y = 0.9483x-1.2874	2	1.055	-1.287	0.994
y = 0.8723x-1.5334	3	1.146	-1.533	0.986
y = 0.8604x-1.791	4	1.162	-1.791	0.980
y = 0.8768x-2.1877	6	1.141	-2.188	0.980
y = 0.9094x-2.5322	8	1.100	-2.532	0.995

Table 4 provides the results of the linear regression analyses, showing the equations for ln(q) versus ln(t) derived from the MMTF model for different packed-bed column heights (1, 2, 3, 4, 6, and 8 cm) of a calcined hard clamshell. The general equation for the linear regression is y = βx + B, where β is the slope and B is the intercept. The slopes (β) for each height vary from 0.985 for the 1 cm bed to 0.9094 for the 8 cm bed, indicating that as the bed height increases, the rate of change in adsorption capacity decreases. The intercept (B) becomes more negative with increasing bed height, ranging from -0.919 for 1 cm to -2.532 for 8 cm, implying that larger bed heights allow for more significant adsorption capacity as time increases. The R^2 values, which measure the goodness of fit for the regression lines, are close to 1, with values between 0.980 and 0.998, indicating a very high correlation between the experimental data and the MMTF model predictions. These results suggest that the MMTF model fits the adsorption data well across all bed heights, with increasing bed height resulting in higher adsorption capacity but a slower adsorption rate. A similar behavior was observed where a multi-port packed-bed column filled with powdered clam shell adsorbent was used for the removal of nickel ions [21]. Their findings indicated that increasing the bed depth (from 5 cm to 25 cm) improved overall adsorption capacity and delayed breakthrough time, while the adsorption rate declined at higher bed depths. The Thomas model, applied in their study, also showed a good fit to the column dynamics ($R^2 > 0.98$), corroborating the relationship between bed depth and mass transfer effects. These observations align with the trends seen in the present study using the MMTF model for phosphate removal, where greater bed depths enhanced overall capacity but reduced adsorption rates, validating the effectiveness of clam shell-based adsorbents and supporting the relevance of mass transfer-driven modeling for both heavy metal and phosphate removal in continuous flow systems.



(a) **(b)**

(c)

Fig. 6 *Variation of mass transfer coefficients for phosphate adsorption using the MMTF model: (a) [kLa]g — global mass transfer factor; (b) [kLa]f — external film mass transfer factor; (c) [kLa]d — internal diffusion mass transfer factor, plotted against the percentage of column outflow for six different adsorbent bed heights*

The three parameters in Fig. 6 illustrate the variations in mass transfer coefficients for [kLa]g, [kLa]f , and [kL a]d as a function of the percentage of outflow for six different bed heights (h=8 cm, h=6 cm, h=4 cm, h=3 cm, h=2 cm, and h=1 cm) in a calcined hard clam shell packed-bed column for the MMTF model. In the Fig. 6(a) the mass transfer coefficient [kLa]g shows a sharp decline as the percentage of outflow increases, particularly for lower bed heights (h=1 cm and h=2 cm), with significantly higher values at lower outflow percentages. The decrease is more gradual for higher bed heights (h=6 cm and h=8 cm), suggesting that thicker beds reduce gas transfer efficiency more slowly. The Fig. 6(b), depicting the mass transfer coefficient [kLa]f, shows much lower magnitudes than [kL a]g, with all depths experiencing a rapid drop in values as outflow reaches 10%. The variation between different bed heights is less pronounced, indicating that liquid film resistance contributes less to the overall transfer. In the Fig. 6 (c), [kLa]d mirrors the trend in [kLa]g, with higher values at lower bed heights, particularly h=1 cm and h=2 cm. The reduction in transfer efficiency as outflow increases is sharp, and differences between bed heights diminish as outflow nears 100%. Overall, lower bed heights show higher initial mass transfer efficiency, which declines rapidly as outflow increases [20]. The Modified Mass Transfer Factor (MMTF) model analysis indicated that while smaller bed depths (1 cm and 2 cm) resulted in faster adsorption rates, larger bed depths (6 cm and 8 cm) allowed for greater overall adsorption capacity over time. The linear regression analysis of the relationship between ln(q) and ln(t) showed high R^2 values (ranging from 0.980 to 0.998), demonstrating that the MMTF model closely fits the experimental data across all bed depths. Additionally, the variations in mass transfer coefficients (kLa) highlighted that lower bed depths exhibited higher initial mass transfer efficiency, which decreased more rapidly as the outflow percentage increased. This suggests that larger bed depths are more effective for long-term adsorption, maintaining efficient mass transfer even as the system approaches breakthrough.

4. Conclusion

This study investigated the potential of calcined hard clam shells as a sustainable and affordable adsorbent for phosphate removal from wastewater. The results demonstrated that deeper adsorbent layers sustained better removal efficiencies over time, while shallow layers reached solute saturation more quickly. Column modeling using the BDST, Thomas, and Modified Mass Transfer Factor (MMTF) models corroborated that although shallow beds exhibited faster initial adsorption rates, deeper beds achieved greater total adsorption capacities and longer operational service times.

Furthermore, the results suggest that calcined hard clam shells offer significant advantages in wastewater treatment applications, particularly in regions with abundant shell waste resources. Their use promotes sustainable waste management and contributes to circular economy initiatives. In practical terms, calcined clam shell beds with greater depths could be implemented in tertiary wastewater treatment facilities to achieve prolonged phosphate removal and mitigate eutrophication risks effectively.

However, potential challenges must be considered for real-world applications, such as maintaining hydraulic performance at greater bed depths, adsorbent regeneration or replacement costs, and ensuring consistent material quality. Further large-scale studies and economic evaluations are recommended to optimize operational parameters and support the scalability of this promising technology. Overall, calcined hard clam shells present a green, cost-effective solution for improving phosphate removal efficiency in wastewater treatment systems, contributing meaningfully to environmental protection and water quality sustainability.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The author confirms sole responsibility for the following: study conception and design, data collection, analysis and interpretation of results, and manuscript preparation.

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