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Phosphorus Removal from Aqueous Solution by Using Calcined Waste Chicken Eggshell: Kinetic and Isotherm Model

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Abstract: Excess phosphorus in water bodies stimulates algal growth and causes eutrophication. Eutrophication is one of the conditions that is a global problem in the environment and affects the quality of water in receiving water. Due to this matter, various wastewater treatment technologies have been developed to solve this problem; however, such technologies incur a high cost for their operation and maintenance. Hence, to seek the eco-friendly element in removing phosphorus from wastewater, this study used calcined waste chicken eggshell to remove phosphorus in an aqueous solution by using adsorbent with different particle sizes (0.075, 0.15, 0.30, 0.60, and 1.18 mm). The calcined waste chicken eggshells were calcined at 800 °C in a furnace and used as adsorbents. The phosphorus adsorption onto calcined waste chicken eggshell data from experiments was fitted to kinetic and isotherm models. Chicken eggshell is an eco-friendly material that has the potential as an adsorbent for removing phosphorus from an aqueous solution, where the highest removal is 98%. The best model for phosphorus removal is the pseudo-second-order (PSO) model, as it fits better with the data and has a high R^2 of 0.9999. Calcined waste chicken eggshells have a multilayer adsorption property, making them a perfect adsorbent with high adsorption capabilities. The application of waste material to adsorb phosphorus from an aqueous solution shows the contribution of eco-friendly waste material use in real adsorption wastewater treatment technologies.

Keywords: calcined waste chicken eggshell; eutrophication; Phosphorus; pseudo-second-order

1. Introduction

Untreated wastewater is one of the global issues of major concern nowadays. Wastewater is produced from everyday household activities from the dishwasher, toilet, sink, and washing machine. The world's water sources, such as lakes and rivers, have much deteriorated due to human activities [1]. About 60% of Malaysia's 90 major lakes have been eutrophicated. Due to the eutrophications problem, Malaysia's effluent standard has been stringent for phosphorus matter in wastewater treatment plant effluent in Malaysia are 5.0 mg

L^{-1} (Standard A) and 10.0 mg L^{-1} (Standard B) to control the excess of phosphorus in receiving bodies [2].

Phosphorus has a few side effects that can harm every living thing, like humans, plants, water, and nature. Even though phosphorus contains some stuff that people use daily and brings benefits, there is no confirmation that it does not bring disadvantages. Without people realizing it, the soap and detergent that people usually use to clean dishes, showers, and laundry may contain phosphorus. The excessive phosphorus in water bodies would cause the eutrophication process, which is the increased growth of algae and large aquatic plants, affecting the decreased levels of dissolved oxygen. High phosphorus levels can harm human and animal health because of the algal toxins produced by the algae blooms. Furthermore, the application of fertilizers in the agriculture sector that contains the elements of phosphorus and nitrogen will encourage the growth of plants. The excessive nutrients flow to the nearest receiving bodies will stimulate the algal growth and enhance the eutrophication in receiving waters.

Excess phosphorus may be handled using various techniques, including adsorption and chemical processes. Chemical extraction incurs significant chemical expenses. Due to the simplicity of the adsorption process and its low cost, waste chicken eggshells can be a potential adsorbent and inexpensive adsorbent for phosphorus removal. Waste chicken eggshells are byproducts of the food manufacturing industry and are usually disposed of in waste disposal areas. They may be used as a low-cost adsorbent material for phosphorus removal from water. Therefore, to solve the phosphorus problem in water, the calcined waste chicken eggshell has been used in this study due to the material's potential to absorb the phosphorus in the water. The waste chicken eggshell contains $CaCO_3$, which can help remove phosphorus from an aqueous solution. Moreover, the calcined waste chicken eggshell through high temperature will provide a catalyst for phosphorus adsorption in water due to containing CaO in calcined adsorbent [3].

Even if many adsorption studies have been used the calcined adsorbents to investigate the phosphorus removal in water, the study on the use of calcined waste chicken eggshell in removing the phosphorus onto the water with verification using kinetic and isotherms model is still not fully understood. The study aimed to determine the feasibility of phosphorus removal from synthetic solution using calcined waste chicken eggshell and determine the best fitting adsorption kinetics and isotherm models for phosphorus adsorption onto calcined waste chicken eggshells from the experimental data.

2. Materials and Methods

2.1. Adsorbents.

About 1.5 kg of chicken eggshell waste was collected to be used as an adsorbent. The chicken eggshells were thoroughly cleaned with tap water and then rinsed with distilled water to remove impurities. They were then dried in an oven at 30 °C for two days. The shells were sieved into five different sizes, which are 1.18, 0.60, 0.30, 0.15, and 0.075 mm [4]. The adsorbent was calcined for 800 °C in a furnace for 2 h. The adsorbent was weighed to 2 g for batch experiments.

2.2. Synthetic solution.

A 10 mg/L PO_4^{3-} the solution was prepared by dissolving 0.1433 g of KH_2PO_4 in 100 mL conical flasks.

2.3. Analytical methods.

DR6000 spectrophotometer (Hach, USA) was used to measure PO_4^{3-} content in the water sample. Fourier transform (FTIR) spectrometer (PerkinElmer, USA) was used to identify the functional group in the samples. D2 PHASER X-Ray diffraction (XRD) instrument (Bruker, USA) was used for identifying the crystalline phases and the chemical composition of the samples. Energy-dispersive X-ray fluorescence (Em-30AX Plus, COXEM, Daejeon, Korea) instrument was used to identify the elemental composition of the adsorbent. Lastly, scanning electron microscopy (EM-30AX Plus, COXEM, Daejeon, Korea) was used to observe the surface morphology of the adsorbent. All the instruments are located in the laboratory of University Tun Hussein Onn Malaysia (UTHM) Pagoh Campus.

2.4. Batch experiments.

For the adsorption studies, 10 conical flasks containing 100 mL of aqueous solutions were used [5]. Therefore, the total volume of aqueous solutions was 1000 mL, and the total adsorbent mass was 20 g of calcined waste chicken eggshell. Each sample was shaken at 170 rpm until it reached equilibrium. Every sample was filtered using a filtration pump to separate the solution from the suspended material, and PO_4^{3-} the content was measured. The data were fitted to kinetics and isotherms models.

2.5. Adsorption kinetics models.

2.5.1. Pseudo-first-order (PFO) kinetic model.

The assumption of the PFO kinetic model is the total rate of unoccupied sites equivalent to occupation sorption sites. Different models for the adsorption of various solutes have been developed, but the applicability and consistency of their linear and nonlinear forms need to be tested. In a PFO model, the graph of ln ($q_e - q_t$) versus t_i gives a straight line [6].

Also referred to Lagergren model, the PFO model describes the adsorption of a solute onto an adsorbent using the first-order process as shown in Eq. 1:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \textbf{Eq. 1}$$

where q_t is the total of adsorbate adsorbed onto the adsorbent at a certain time t (mg/g), q_e is the equilibrium adsorption potential (mg/g), and k_1 as the constant rate (min) [7]. According to Eq. 1, the integral from t = 0 to t = t and $q_t = 0$ to $q_t = q_t$ yields a linear representation of PFO, which is shown as Eq. 2:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \textbf{Eq. 2}$$

2.5.2. Pseudo-second-order (PSO) kinetic model.

The PSO kinetic model assumes that the total solute adsorbed is equal to the number of accessible sites on the adsorbent (Eq. 3) [8]. Furthermore, the reaction rate is proportional to the solute concentration on the surface of the adsorbent, and the driving force is equal to the number of active sites.

$$\frac{t_i}{q_t} = \frac{1}{k_2 q_e^2 + \frac{t_i}{q_e}} \quad \textbf{Eq. 3}$$

where q_t (mg/g) denotes the amount of phosphorus adsorbed during the adsorption period, q_e denotes the amount of phosphorus adsorbed at equilibrium (mg/g), k_2 denotes the pseudo-second-order rate constant (min), and t_i denotes the adsorption duration (min) [9].

The slope and intercept of the plot t_i/q_t versus t_i can be used to determine the values of k_2 and q_e, respectively (Table 1). If the curve plotted from t_i/q_t versus t_i is a straight line, the adsorption kinetics obeys a PSO model [10]. The linear PFO and PSO models were used to evaluate the sorption feature, optimum condition, and possible rate-controlling stage during the adsorption kinetic tests, as shown in Table 1. These models have been effectively extended to the PO_4^{3-} adsorption in the aqueous solution.

Table 1. Kinetic model parameters.

Kinetic model	Linear form	Plot	Parameters
Pseudo-first-order (PFO)	$\ln(q_e - q_t) = \ln(q_e) - k_1 t_1$	$\ln(q_e - q_t)\ vs\ t_i$	$q_e(mg\ g^{-1})$ $k_1(min^{-1})$ R^2
Pseudo-second-order (PSO)	$\frac{t_i}{q_1} = \frac{1}{k_2 q_e^2} + \frac{t_i}{q_e}$	$\frac{t_i}{q_t}\ vs\ t_i$	$q_e(mg\ g^{-1})$ $k_2(min^{-1})$ R^2

2.6. Adsorption Isotherms models.

Adsorption is commonly described through isotherms that combine the amount of adsorbate on the adsorbent. In this study, the data were fitted to Freundlich and Langmuir isotherm models to determine the best model that fits the adsorption process [11]. The quantity of adsorbate adsorbed per unit weight of the adsorbent was determined [12].

2.6.1. Freundlich isotherm.

The Freundlich isotherm can be stated as an empirical model, as shown in Eq. 4:

$$ln\, q_e = \ ln\, K_F + \frac{1}{n} ln\, C_e \quad \textbf{Eq. 4}$$

where q_e is the amount adsorbed per amount of adsorbent at equilibrium (mg/g), C_e is the concentration of equilibrium state (mg/L), and K_f and n are the adsorption capacity and adsorbent intensity, respectively.

2.6.2. Langmuir isotherm.

The Langmuir model also has a nonlinear form in which the equation is almost the same as the Freundlich model, although the Langmuir model has q_{max}, which is the maximum adsorbent capacity. According to the Langmuir model, solute adsorption is due to monolayer adsorption on the surface of the adsorbent. The Langmuir model can be expressed in linear form, as shown in Eq. 5:

$$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}} \quad \textbf{Eq. 5}$$

where C_e is the adsorbate concentration at equilibrium (mg/g), the linear forms for both models are summarised in Table 2.

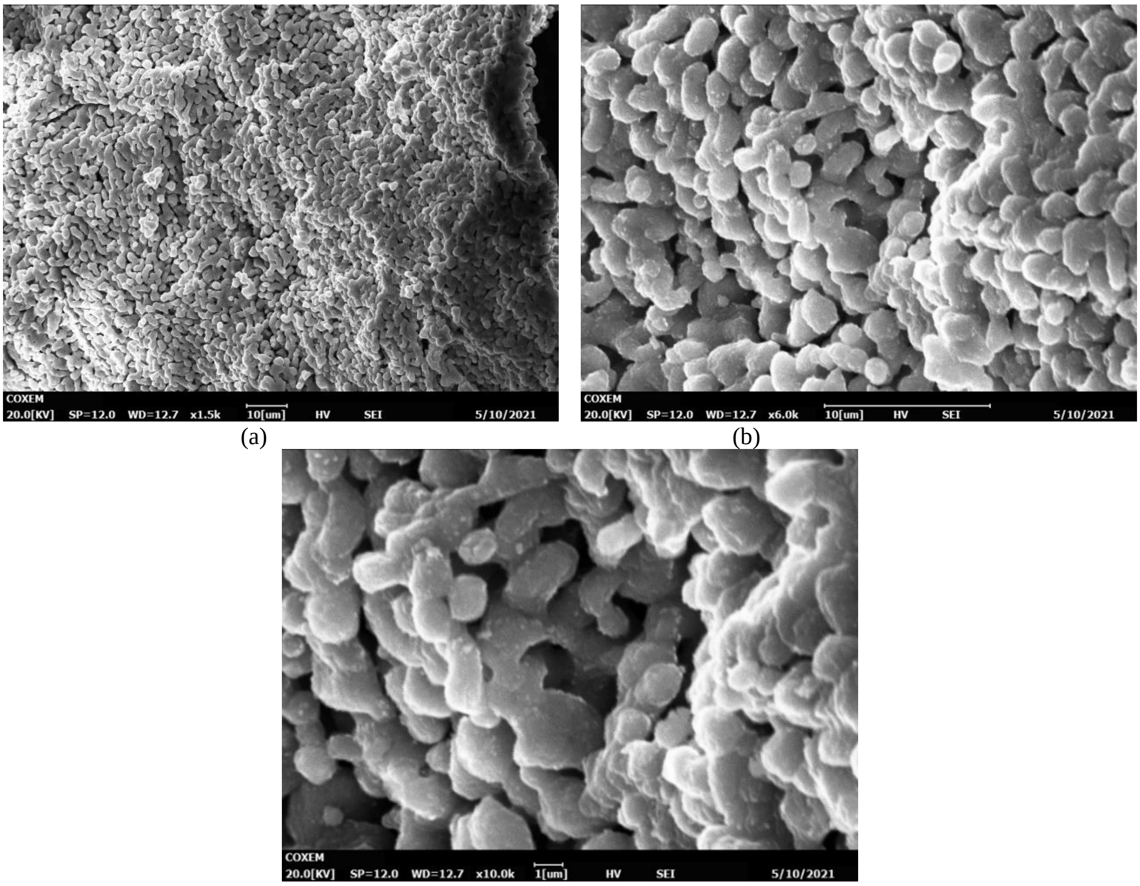
Table 2. Isotherm model parameters.

Isotherm models	Linear form	Plot	Parameter
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} lnC_e$	$\ln(q_e)\ vs\ (C_e)$	$K_F\ (mg/g)$ $\frac{1}{n}$ R^2
Langmuir	$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}}$	$\frac{1}{q_e}\ vs\ \frac{1}{C_e}$	$q_{max}\ (mg/g)$ $K_L\ (mg/g)$ R^2

3. Results and Discussion

3.1. Physical and chemical characteristics of calcined waste chicken eggshell.

Calcined waste chicken eggshells' physical and chemical properties were investigated to determine its potential as an adsorbent for phosphorus. The chemical compositions of calcined waste chicken eggshell as determined from the SEM analysis are Ca (53.92%), O (37.61%), Mg (1.33%), C (5.98%), Al (0.27%), Cu (0.45%), Na (0.20%), K (0.08%), and Sr (0.15%), as shown in Table 3. Ca and O had the highest composition percentages. These elements can remove and adsorb much phosphorus quickly [13]. Generally, raw waste chicken eggshell contains calcium carbonate that potentially removes phosphorus in the water. However, the calcination of adsorbents with high temperatures will enhance phosphorus removal due to the existence of CaO. The process of adsorption occurs in physical and chemical reactions simultaneously. Physical absorption occurs when Van der Waals forces interaction with the porous surface due to calcine adsorbent and calcine adsorbent Ca^{2+} can occur the chemical or electrostatic interaction due to sharing electrons in solution.



(a) (b)

(c)

Figure 1. SEM photomicrograph of calcined waste chicken eggshell: (**a**) 1500× magnification, (**b**) 6000× magnification, and (**c**) 10000× magnification.

Table 3. Composition of the Calcined Waste Chicken Eggshell (wt.%).

Ca	*O*	*Mg*	*C*	*Al*	*Cu*	*Na*	*K*	*Sr*
53.92%	37.61%	1.33%	5.98%	0.27%	0.45%	0.20%	0.08%	0.15%

The surface morphology of calcined waste chicken eggshell for 1.18mm particle size of adsorbent was investigated using SEM at magnifications 1500×, 6000×, and 10000×, as shown in Figure 1. As illustrated in Figure 1(b) and Figure 1(c), the surface characteristics of calcined waste chicken eggshells are somewhat rough [14]. At 10000× magnification, the calcined waste chicken eggshell has tiny holes on its surface, as shown in Figure 1(c).

The XRD pattern in Figure 2 shows the adsorbent contained lime ($CaCO_3$) is the major component of calcined waste chicken eggshell, and the other components on the XRD pattern are oxygen (O_2), sodium peroxide (Na_2O_2), portlandite ($Ca(OH)_2$), magnesium (Mg), and periclase (MgO). Several studies have found that $CaCO_3$ has strong adsorption capabilities for PO_4^{3-} ions [15].

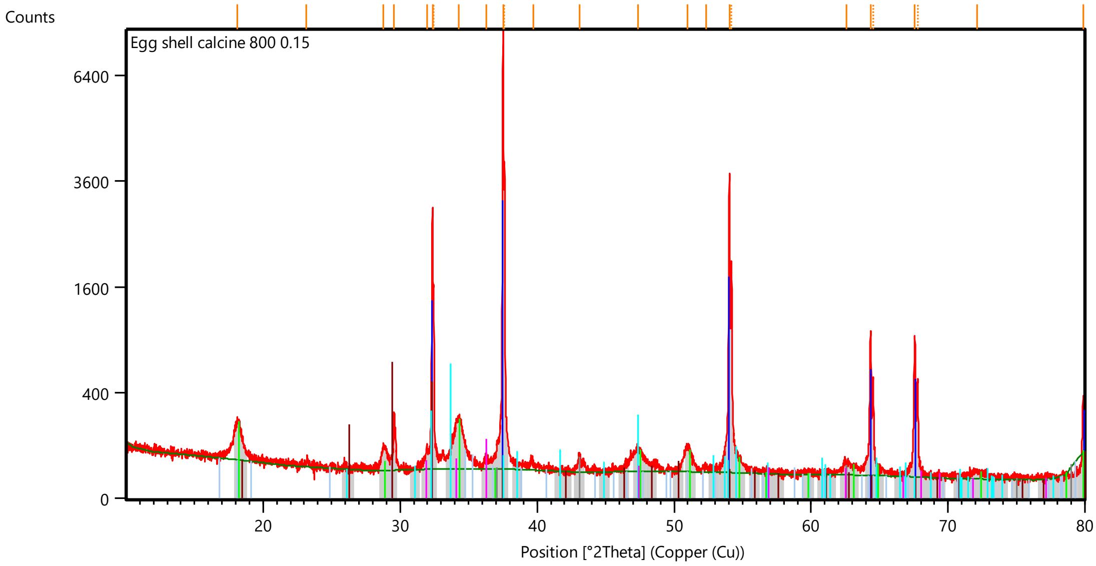


Figure 2. X-ray diffraction patterns of calcined waste chicken eggshell.

According to the FTIR spectra shown in Figure 3, PO_4^{3-} adsorbed calcined waste chicken eggshells were measured over a range of 800 to 3700 cm^{-1} and compared to gather information on surface functional groups and changes [16]. FTIR analysis is important to identify the chemical bond of organic components in adsorbents, and Table 4 shows the FTIR spectra of calcined waste chicken eggshells before and after adsorption of PO_4^{3-} ions. The original and position of the surface functional groups influence the position and shape of the PO_4^{3-} stretching band in the FTIR spectra of calcined waste chicken eggshells. The tetrahedral PO_4^{3-} molecules are coordinated.

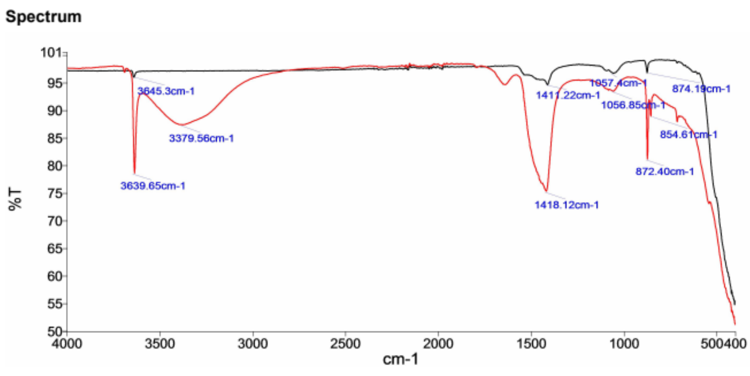


Figure 3. The FTIR spectra of calcined waste chicken eggshells adsorbent (1.18mm) before and after PO_4^{3-} adsorption.

Due to ion exchange between the PO_4^{3-} molecules adsorbed onto the surface of calcined waste chicken eggshells and the C–O functional groups, the frequency spectrum increased by 1.79 cm^{-1} (874.19–872.40), 0.55 cm^{-1} (1057.4–1056.85), and 6.9 cm^{-1} (1418.1–1411.22). The stretching is affected because of the vibrations [17].

Table 4. FTIR spectra of calcined waste chicken eggshells adsorbent (1.18mm) before and after adsorption of PO_4^{3-} ions.

Frequency spectrum (cm^{-1})			Detection of functional group	Reference
Before adsorption	**After adsorption**	**Difference**		
3636.45	3645.3	8.85	O–H stretching band	[26]
1411.22	1418.12	6.9	N–O stretching band	[28]
1056.85	1057.4	0.55	C–O stretching band	[13], [21]
872.40	874.19	1.79	C–O stretching band	[13], [21]

3.2. Phosphorus adsorption.

Phosphorus adsorption on calcined waste chicken eggshells was measured over time to determine the equilibrium-corresponding contact duration [18]. This is because adsorption kinetics presents the relationship between measuring the adsorption uptake according to time at the same pressure or concentration. Also, employed to measure the amount of diffusion adsorbate onto pores [19]. At the beginning of the adsorption, the first few minutes can be defined rapidity of adsorption kinetic presence in a large amount due to the active surface sites and those remaining after a certain period [20]. This adsorption transition method from the liquid phase to the solid phase [21].

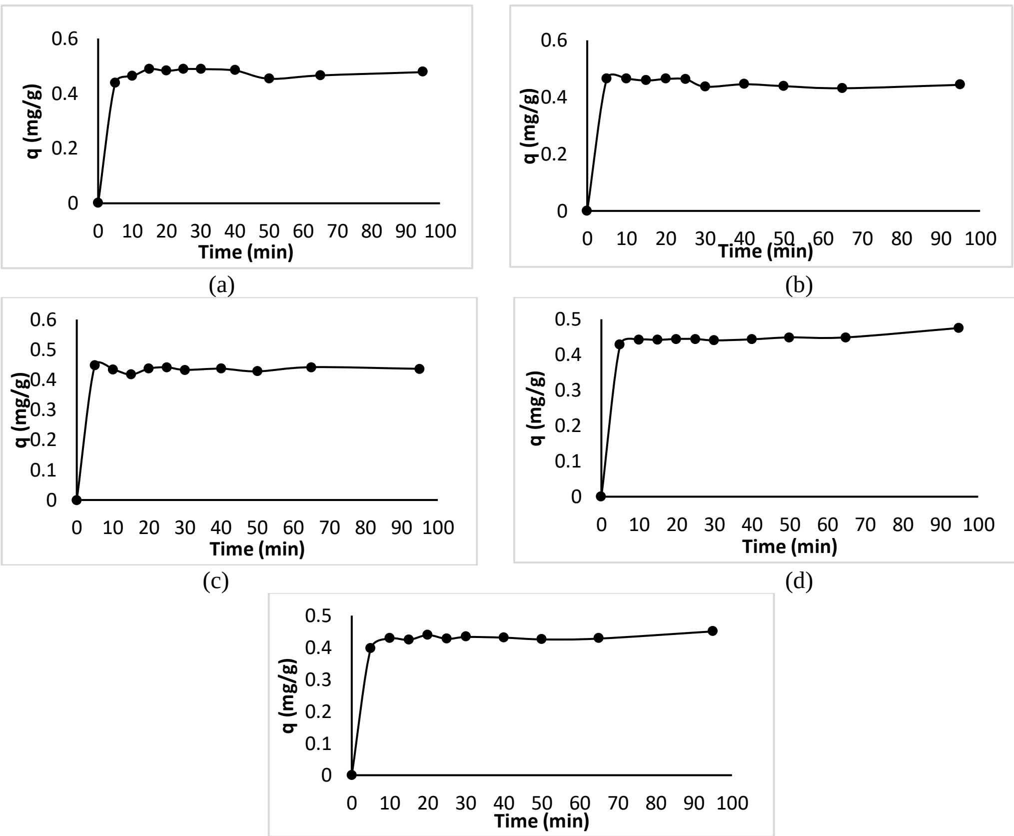


Figure 4. The adsorption potential of calcined waste chicken eggshell for sizes (**a**) 1.18, (**b**) 0.60, (**c**) 0.30, (**d**) 0.15, and (**e**) 0.075 mm.

Adsorption capacity performance is the amount of adsorbate adsorbed per unit mass. In this study, adsorption ability is the total value of the calcined waste chicken eggshells used to adsorb phosphorus in the wastewater. The adsorption potential of each particle size. The adsorption capacity is calculated as shown in Eq. 6:

$$q = \frac{C_i - C_f}{m} x\, V \qquad \textbf{Eq. 6}$$

By using the formula, the adsorption potential of the calcined waste chicken eggshells was determined. The adsorption data for the sample from the start until equilibrium are plotted and shown in Figure 4.

Figure 4 shows the adsorption performance for five different sizes of calcined waste chicken eggshells. The number of adsorbents (q) can be used to see how many adsorbents were adsorbed during the process. Ten flasks were used for each size to determine the q_e, which is the amount of phosphorus adsorbed at equilibrium. For each size, the values of q_e were 0.4885 mg/g (1.18 mm), 0.4655 mg/g (0.60 mm), 0.437 mg/g (0.30 mm), 0.4425 mg/g (0.15 mm), and 0.428 mg/g (0.015 mm).

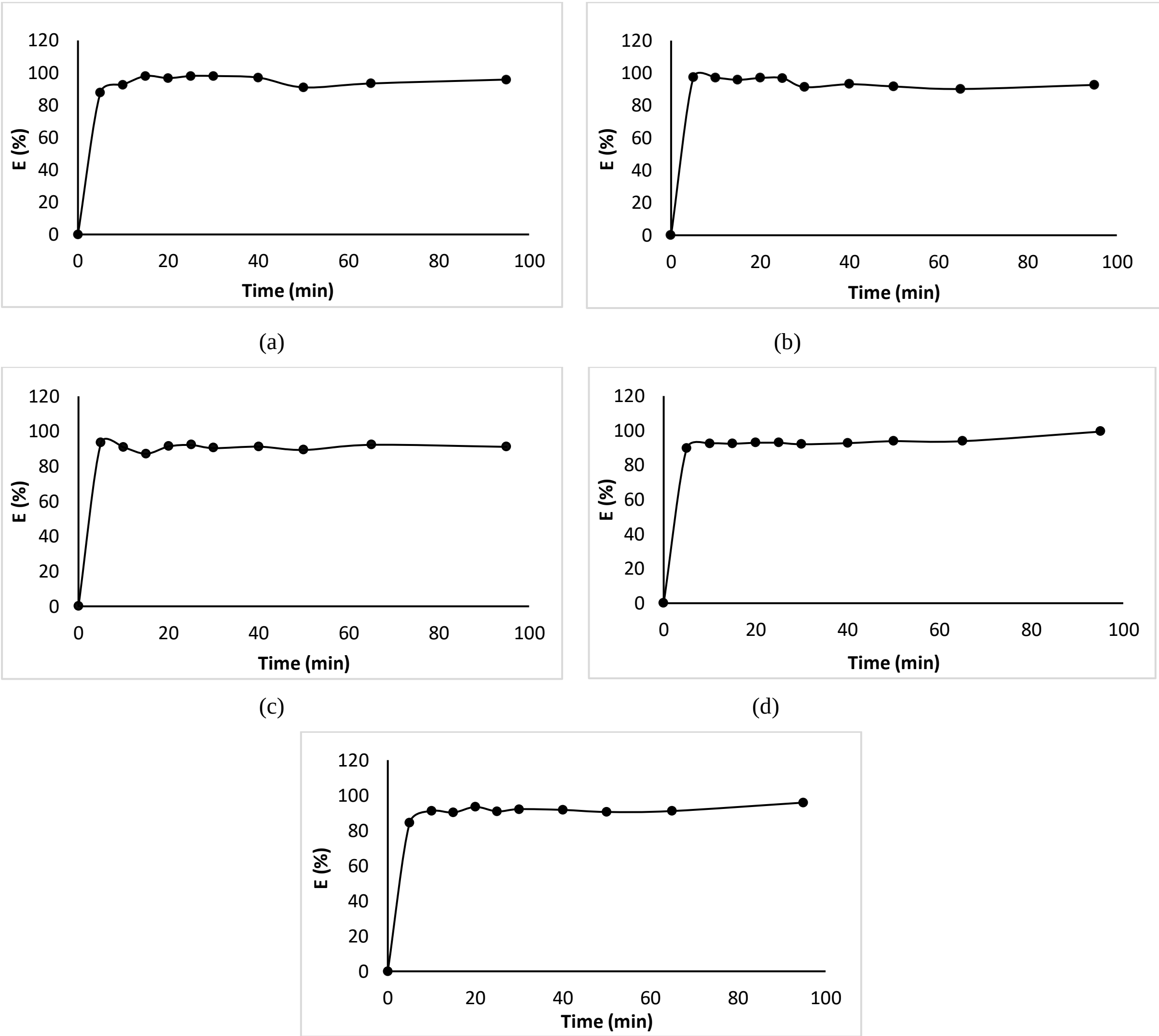


Figure 5. The removal efficiency of calcined waste chicken eggshell for sizes (**a**) 1.18, (**b**) 0.60, (**c**) 0.30, (**d**) 0.15, and (**e**) 0.075 mm.

This removal efficiency of the sample was also determined in this study. This shows how effective the calcined waste chicken eggshell is as an adsorbent to remove phosphorus from wastewater. The removal efficiency was calculated by using Eq. 7:

$$E = \frac{Ci-Cf}{Ci} \times 100\% \quad \textbf{Eq. 7}$$

The phosphorus removal efficiency of calcined waste chicken eggshell was plotted and shown in Figure 5.

Figure 5 shows the phosphorus removal efficiency by five different sizes of calcined waste chicken eggshells. This removal efficiency (E) can be used to see how much phosphorus was removed during the process [22]. This analysis aimed to determine the efficiency of calcined waste chicken eggshells as an adsorbent to remove phosphorus from the sample. The data were chosen from the q_e values, which show the best removal efficiency for each class. The removal efficiency (E) for each size were 98% (1.18 mm), 97% (0.60 mm), 91% (0.30 mm), 92% (0.15 mm), and 91% (0.015 mm). The 1.18 mm particles size showed the highest removal efficiency compared to other sizes. It showed the ability of 1.18mm particle size of adsorbent to adsorb the phosphorus due to availability on the binding surface of the adsorbent. However, the result supported the presence of the hydroxy group, which is O–H compounds in adsorbents that can engage and increase the electrostatic bonding with molecules in calcined waste chicken eggshell.

3.3. Pseudo-first-order (PFO) kinetic model.

The PFO and PSO are commonly used in adsorption kinetics. These two models are utilized to determine whether the reaction mechanism is chemical or physical [23]. According to Eq. 8, F_e value can be calculated from the data obtained, and the value of the kinetic model should have the highest R^2 and smallest F_e value from PFO and PSO model analysis.

$$F_e = \sqrt{\left(\frac{1}{n-p}\right) \cdot \sum_i^n \left(q_{t(\exp)} - q_{t(theo)}\right)} \quad \textbf{Eq. 8}$$

The value of n represents the number of measurements, p represents the number of kinetic parameters, $q_{t(exp)}$ and $q_{t(theo)}$ is the experimental and theoretical adsorption capacity (mg/g), respectively. The graph obtained when the data were fitted to the pseudo-first-order model is shown in Figure 6.

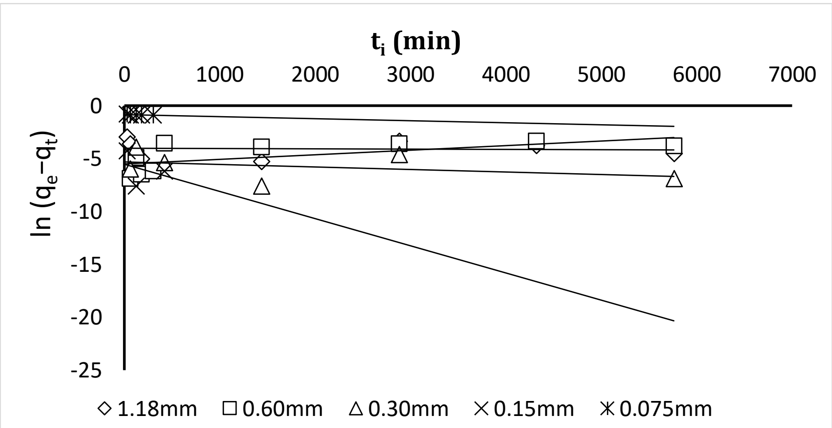


Figure 6. Pseudo-first-order model graph for calcined waste chicken eggshell.

As shown in Table 5, the adsorbent size of 0.60–1.18 mm shows a good phosphorus adsorption capability and high efficiency because it has the highest R^2 value. In contrast, the adsorbent size of 1.118–2.36 mm has the highest F_e value, which indicates that this size is not capable of adsorbing phosphorus well.

Table 5. Kinetics table of pseudo-first-order model.

Particle Size (mm)	$q_{e(theo)}$ (mg g^{-1})	k_1 (min^{-1})	R^2	F_e	$q_{e\ (exp)}$ (mg g^{-1})
1.18–2.36	0.0178	0.00005	0.0052	2.7292	0.4885
0.60–1.18	0.0040	0.00040	0.4196	2.6049	0.4655
0.30–0.60	0.0049	0.00020	0.1470	-	0.4370
0.15–0.30	0.0039	0.00026	0.0983	2.5722	0.4425
0.075–0.15	0.4280	0.00020	0.3068	2.4515	0.4280

3.4. Pseudo-second-order (PSO) kinetic model.

The pseudo-second-order model was the rate-limiting step involving chemisorption, where phosphorus removal from a solution is due to physicochemical interactions between the two phases [24]. This model provides the best correlation of the experimental data, and the adsorption mechanism is chemically rate-controlling so that it can be referred to as chemisorption. Figure 7 shows the resulting graph when the data were fitted to the pseudo-second-order model.

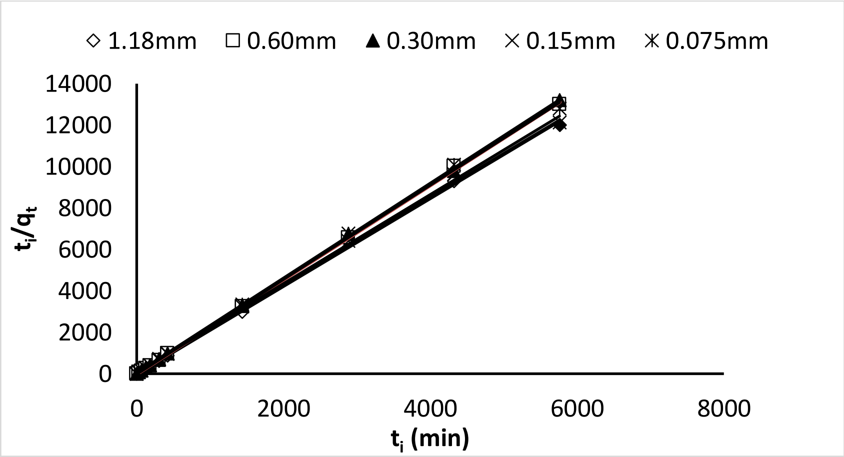


Figure 7. Pseudo-second-order model graph for calcined waste chicken eggshell.

As shown in Table 6, the 0.60–1.18 mm adsorbent size shows a good capability to adsorb the phosphorus with high efficiency, similar to the pseudo-first-order model. Although the R^2 value for 0.60–1.18 mm is high and closer to 1 (0.9998), the 0.075–0.15 mm size has the highest R^2 value, 0.999. This shows that the pseudo-second-order model fits better for this adsorption than the pseudo-first-order model [25].

Table 6. Kinetic table for pseudo-second-order model for calcined waste eggshell.

Particle Size (mm)	$q_{e(theo)}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2	F_e	$q_{e\ (exp)}$ (mg g^{-1})
1.18–2.36	0.4718	0.8943	0.9994	2.6877	0.4885
0.60–1.18	0.4389	-0.6284	0.9998	0.4200	0.4655
0.30–0.60	0.4367	0.8331	0.9999	0.5490	0.437
0.15–0.30	0.4651	0.0899	0.9988	0.5709	0.4425
0.075–0.15	0.4412	0.1341	0.9990	0.7063	0.4280

Table 5 and Table 6 show the kinetic parameters for PFO and PSO. The R^2 for the PSO model is 0.9999, which is higher than the R^2 for the PFO model (0.4196). From this analysis, the PSO model is the best-fitted model for than PFO model due to its high R^2 value and the lowest value of F_e.

3.5. Adsorption isotherm model.

The Freundlich and Langmuir models were investigated in this experiment. At maximal coverage, the Langmuir model assumes a monomolecular layer on the surface of adsorbents [26]. This indicates that the adsorbed molecules are not stacked. In contrast, the Freundlich isotherm is not constrained in this way. Instead, the Freundlich adsorption isotherm quantifies the fluctuation in the amount of gas adsorbed by a unit mass of solid adsorbents as a system's pressure varies at a fixed temperature [27].

Table 7. Calcined waste eggshells adsorption isotherm.

Freundlich model			Langmuir model		
n	**K_f (mg g^{-1})**	**R^2**	**q_{max} (mg g^{-1})**	**K_L (L mg^{-1})**	**R^2**
−0.0798	2.2862×10^{-5}	0.9377	0.0282	−2.38778	0.8526

As shown in Table 7, the Freundlich model is a better fit for phosphorus adsorption by calcined waste eggshells. This is because the value of R^2 in the Freundlich model (0.9377) is higher than that of the Langmuir model (0.8526). The R^2 value for the Freundlich model is closer to 1 and thus is a better fit to explain phosphorus adsorption.

4. Conclusions

In this study, the use of calcined waste chicken eggshells as an adsorbent to remove phosphorus from the solution was investigated. This study has shown the potential of calcined waste chicken eggshell adsorbent for application in the wastewater treatment system to reduce phosphorus content in effluents. The high calcium carbonate content is the agent and main key to removing phosphorus from the wastewater. Calcined waste chicken eggshell is an effective adsorbent, as seen from the high phosphorus removal of 98%. Besides, waste chicken eggshell is an environmentally friendly adsorbent because they can be easily obtained and available in large quantities. The adsorption kinetics model fitted verified PSO kinetic model in which the value of R^2 is 0.9999.

Furthermore, waste chicken eggshells have a multilayer adsorption property, making them a perfect adsorbent with high adsorption capabilities. The analysis of kinetic and isotherm models can verify the theoretical and experimental approach; therefore, it is important to develop engineering predictions on wastewater treatment adsorption technologies. In addition, the application of waste material to adsorb phosphorus from an aqueous solution shows the contribution of eco-friendly waste material use in real adsorption wastewater treatment technologies.

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Conflicts of Interest

The authors declare no conflict of interest.

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