Raw Duck Eggshells to Adsorb Nitrate from Groundwater: Kinetic and Isotherm Studies

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Nitrate is an essential element for plant and animal growth. However, excess nitrate in groundwater may impact the environment and human health. Even though a variety of treatments for nitrate are available, there is still a need to verify the theoretical and experimental data using kinetic and isotherm models. This study aimed to investigate the performance of raw duck eggshells in removing nitrate from groundwater. The batch experiment used different adsorbent masses (2, 4, 6, 8, 10 g) in 100 mL aqueous solution for a certain time. The theoretical and experimental data were verified using kinetic (pseudo-first-order and pseudo-second-order) and isotherm (Langmuir and Freundlich) model studies. The equilibrium nitrate adsorption time obtained was 1440 min and the highest nitrate removal efficiency was 49.3 % for a 10 g mass of adsorbent with an adsorption capacity of 0.0365 mg/g. The kinetic verification model for pseudo-second-order fit well and had a correlation coefficient, R^2 of 0.9998, which showed that chemical sorption occurred within the adsorption process. The Langmuir isotherm model was the best fit, with an R^2 value of 0.5210. This indicated single layer adsorption on specific surface sites of adsorbent. Contour prediction was developed to simplify the estimation of removal efficiency with different initial concentrations using the required adsorbent mass. The results highlight the potential of raw duck eggshells in removing nitrate from water, and is an eco-friendly method for future water treatment.

Keywords: Raw duck eggshells, nitrate, isotherm, kinetic models, groundwater

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Nitrate is among the most prevalent chemical pollutants in groundwater [1]. Chemically, nitrate refers to the nitrate ion (NO_3^-), a negatively charged polyatomic ion composed of one nitrogen and three oxygen atoms. It is the oxidized and most stable form of nitrogen in the natural nitrogen cycle, typically derived from both natural and anthropogenic sources such as fertilizer runoff, decaying organic matter, and wastewater discharge. Nitrate does not exist as a neutral element but is commonly found in the form of ionic compounds, including sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), and calcium nitrate ($Ca(NO_3)_2$). These compounds readily dissolve in water and release nitrate ions, which are highly soluble and mobile in groundwater. In aqueous systems, nitrate remains stable under aerobic conditions and does not easily volatilize or degrade, making it highly persistent and mobile in groundwater [2]. Excessive nitrate levels can be detrimental to health, increasing the risk of certain cancers and thyroid diseases [3]. The problem has become more severe with global development, as growing demand for food and water resources contributes to escalating contamination levels [4].

In groundwater systems, the nitrate ion represents the final oxidation product of various nitrogen transformations. Other nitrogen species, such as nitrite (NO_2^-) and ammonium (NH_4^+), are less stable intermediates in the nitrogen cycle and can easily convert into nitrate under oxidizing environmental conditions. This interconversion explains why nitrate is often the dominant and most persistent contaminant in groundwater compared to other reactive nitrogen forms. Nitrate naturally occurs at moderate concentrations as a by-product of the decomposition of nitrogen-containing organic matter found in soil and rocks [5].

While natural processes contribute to baseline nitrate levels, human agricultural activities have significantly intensified nitrate contamination. The excessive application of nitrogen-based fertilizers, including those containing nitrate salts such as sodium nitrate ($NaNO_3$) and potassium nitrate (KNO_3), as well as fertilizers that produce nitrate through microbial nitrification processes such as urea and ammonium-based compounds, combined with the improper management of livestock waste, contributes substantial amounts of nitrate to the environment. During rainfall or irrigation, residual fertilizer and manure leach into the soil, infiltrating aquifers and contaminating groundwater. This process results in concentrations that exceed natural background levels, particularly in intensively farmed land or arid regions where water circulation is limited [6].

According to the World Health Organization (WHO), the permissible nitrate concentration in drinking water is 50 mg/L, established to protect public health and minimize the risks associated with excessive intake [7]. Similarly, the United States Environmental Protection Agency (EPA) has set the Maximum Contaminant Level (MCL) for nitrate at 10 mg/L as NO_3^--N [8]. Although these standards were designed primarily to prevent infant methemoglobinemia, other health concerns such as cancers and reproductive issues have also been reported [9].

Nitrate, though an essential plant nutrient, poses a serious risk when found in high concentrations. In the body, nitrate can be converted into nitrite (NO_2^-), which reacts with amines to form carcinogenic nitrosamines [10]. Several studies have reported possible links between long-term nitrate exposure and specific cancers or birth abnormalities, especially when nitrate ingestion promotes N-nitroso compound formation [11]. However, findings on reproductive effects remain inconsistent. While some studies show no clear connection between nitrate exposure and congenital disorders, others suggest associations with preterm births and certain birth defects [12].

Although the evidence is not yet conclusive, some research indicates that pregnant and breastfeeding women may be more vulnerable to nitrate exposure due to physiological changes that affect metabolism and oxygen transport [13]. Hence, these groups should be given special consideration in water quality monitoring and public health protection.

Excessive nitrate levels have been reported in various regions. For instance, the Gaza Strip showed nitrate concentrations ranging from 40 mg/L to over 300 mg/L [14], exceeding WHO guidelines [15]. In Iowa, a cohort study found that individuals consuming private well water with nitrate levels below 10 mg/L NO_3^--N still exhibited elevated methemoglobin levels, suggesting that even low-level exposure can pose risks [11]. Global nitrate concentrations are expected to rise due to intensive fertilizer use and livestock farming, underscoring the need for effective mitigation strategies [16].

Several studies have reported the presence of nitrate in groundwater from different regions and sources. In rural wells of the Ceanu Mare commune, Cluj County, Romania, nitrate concentrations ranged from 39.7 to 48 mg/L, which corresponds to 96 % of the EU/WHO permissible limit of 50 mg/L [17]. In the riverside plains of China, nitrate pollution was also significant, with 40.5 % of groundwater samples in the wet season and 28.6 % in the dry season exceeding the national Class III standard of 20 mg/L [18]. Furthermore, a high-resolution case study in Chongqing, China, revealed that while most groundwater samples contained less than 1 mg/L of nitrate, localized regions in the southeast, northeast, and central karst valley areas recorded higher proportions exceeding 10 mg/L, accounting for 1.89 %, 0.91 %, and 0.38 % of samples, respectively [19]. These findings demonstrate that nitrate contamination levels vary according to land use, hydrogeological conditions, and anthropogenic activities.

Efficient and affordable nitrate removal techniques are therefore essential. Physical and chemical methods such as reverse osmosis, ion exchange, and electrodialysis have been applied but often face challenges related to high operating costs, poor selectivity, and maintenance requirements [20]. Adsorption offers a simpler and more sustainable alternative when environmentally friendly materials are used. Calcium-based adsorbents, such as eggshell-derived CaO, have shown promise for nitrate removal [21]. Duck eggshells, composed of approximately 92.57% calcium carbonate, are abundantly available as domestic and industrial waste and can be converted into low-cost bio-adsorbents for treating contaminated water [22]. The present study, therefore, provides a sustainable approach for mitigating nitrate pollution in contaminated groundwater sources.

The novelty of this research lies in the utilization of raw duck eggshells, an abundant and low-cost biogenic waste, as a promising adsorbent for eliminating nitrate from aqueous solutions. While various calcium-based materials such as chicken eggshells and calcined shells have been studied, limited research has focused on the direct application of raw duck eggshells without pretreatment. This study contributes new insights into the adsorption performance, kinetic behaviour, and isotherm characteristics of raw duck eggshells, thereby establishing their potential as an eco-friendly adsorbent for mitigating nitrate contamination in groundwater. This study investigates the efficiency of raw duck eggshells as an adsorbent for the removal of nitrate from water. The parameters evaluated include adsorbent mass, initial nitrate concentration, and

contact time. Adsorption behaviour is analyzed using kinetic and isotherm models, including pseudo-first-order, pseudo-second-order, Freundlich, and Langmuir models, to compare experimental and theoretical data.

MATERIALS AND METHODS

Preparation of Adsorbent

The adsorbent was cleaned by sequential washing with tap water and deionized water to ensure the removal of impurities. The raw duck eggshells were then sun-dried for two days to ensure complete dehydration, followed by oven-drying at 30 °C for an additional two days to eliminate residual moisture. After drying, the eggshells were crushed using a mortar and pestle to obtain a finely powdered material, which was sieved to obtain particles within the 1.18–2.36 mm size range.

This particle size range was selected based on previous studies that reported it as optimal for eggshell-based adsorbents, providing an adequate surface area for effective adsorption while preventing excessive compaction or clogging during filtration [19]. In the present study, the particle size was kept constant to ensure comparability with earlier findings and to focus on other key variables such as adsorbent dosage, initial nitrate concentration, and contact time. The effect of particle size on adsorption efficiency was therefore not investigated further.

Preparation of Aqueous Solution

Potassium nitrate (KNO_3) was used to prepare the stock solution. The required mass of KNO_3 was calculated based on the molecular weight relationship between KNO_3 (101.1023 g/mol) and the nitrate ion, NO_3^- (62.004 g/mol). To obtain a 100 mg/L NO_3^- solution, the equivalent amount of KNO_3 was determined using the following equation:

$$Mass\ of\ KNO_3 = \frac{101.1023 \frac{g}{mol}}{62.004 \frac{g}{mol}} \times 0.1 = 0.1631\ g$$

Thus, 0.1631 g of KNO_3 was accurately weighed, dissolved in a small volume of deionized water, and diluted to a final volume of 1 L in a volumetric flask to produce the 100 mg/L stock nitrate solution. This stock solution was subsequently diluted with deionized water to obtain working concentrations of 50 mg/L, 25 mg/L, 20 mg/L, 15 mg/L, 10 mg/L and 5 mg/L NO_3^-–N.

Batch Experiment Studies

Batch adsorption experiments were conducted in two stages to evaluate the performance of the raw duck eggshells in removing nitrate. The first batch focused on predicting the removal efficiency based on the initial nitrate concentration and adsorbent mass, while the second batch examined the adsorption kinetics and isotherm behaviour using groundwater samples.

In the first batch, synthetic nitrate solutions were prepared as described in the previous section. Two main variables were examined in this study, namely the initial nitrate concentration at 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L and 25 mg/L, and the adsorbent mass at 2 g, 4 g, 6 g, 8 g and 10 g. The particle size of the adsorbent was maintained within the range of 1.18 mm to 2.36 mm, while the solution volume was fixed at 100 mL throughout the experiment to ensure consistent conditions. Each mixture was agitated in an orbital shaker at a speed of 170 rpm for a total duration of 4320 minutes, equivalent to 72 hours, to achieve adsorption equilibrium.

All batch adsorption experiments were conducted at a controlled room temperature of 25 ± 2 °C. This temperature was selected as it represents standard laboratory conditions and has been reported in the literature to maintain stable adsorption kinetics for calcium carbonate–based adsorbents without altering their structural integrity. Conducting the experiments under this moderate and consistent temperature ensured that any variations in nitrate removal efficiency were primarily due to adsorbent mass and contact time rather than thermal effects. After shaking, the samples were filtered using a vacuum pump, and the nitrate concentration in the filtrate was determined using a DR6000 UV–Vis spectrophotometer. The resulting data were used to construct a prediction contour illustrating the relationship between nitrate removal efficiency, initial concentration, and adsorbent mass.

The second batch experiment was conducted using groundwater samples collected from Kelantan, Malaysia, following a similar procedure. The same range of particle sizes, between 1.18 mm and 2.36 mm, and the same adsorbent masses of 2 g, 4 g, 6 g, 8 g and 10 g were employed. Samples were collected at various contact times (30 minutes, 120 minutes, 300 minutes, 1440 minutes and 4320 minutes) to examine the adsorption rate and equilibrium behaviour. The resulting data were analysed using pseudo-first-order and pseudo-second-order kinetic models, as well as the Langmuir and Freundlich isotherm models, in order to describe the adsorption mechanisms and evaluate the reliability of the experimental results.

Analytical Methods

The cadmium reduction method was used to determine nitrate content. This method was prepared in the following manner using NitraVer 6 Reagent Powder Pillow [23]. A HACH DR 6000 UV-VIS Spectrophotometer was used to analyze the initial and final concentrations of nitrate in aqueous

solutions utilizing potassium nitrate. The surface morphology of the membranes of fresh duck eggshells was determined using a COXEM EM-30AX PLUS SEM. A Perkin Elmer Spectrum TWO FTIR Spectrophotometer was used to determine the shell's functional groups before and after the experiments. Lastly, a BRUKER D2 Phaser Benchtop XRD was used to characterize the shell's crystallization or crystal phase composition by XRD analysis.

Kinetic Model Study

Adsorption is the process through which solute molecules adhere to an adsorbent. The adsorption system is completed in a batch or column configuration. Adsorption kinetics describes the rate at which a solute is retained or released from an aqueous solution onto a solid–liquid interface under specific experimental conditions such as adsorbent dosage, temperature, flow rate, and pH. Both physical and chemical processes are involved during adsorption. Attractive forces cause physical adsorption, whereas chemical adsorption is caused by the creation of a strong connection between the solute and the adsorbent, which results in electron switching. The Pseudo-First-Order model (PFO) explains the adsorption of the solute on the adsorbent by a first-order mechanism, as in Eq. 1 [23].

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

where q_t is the adsorbent at time t (mg/g), q_e is the equilibrium adsorption capacity (mg/g), and k_1 is the rate constant per minute.

The Pseudo-Second-Order (PSO) model implies that the rate of solute adsorption is proportional to the adsorbent's accessible sites [23]. As demonstrated in Eq. 2, the reaction rate is proportional to the amount of solute on the adsorbent surface, and the kinetics is proportional to the number of active sites on the adsorbent.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad \textbf{Eq. 2}$$

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

where k_2 is the PSO rate constant. Applying the integral limits for t (o, t) and q_t (o, q_t), the linearised form of PSO is shown in Eq. 3.

Isotherm Model Study

The Langmuir isotherm is theoretical, while the Freundlich isotherm is empirical [23]. The Langmuir is the best model to identify the adsorption equilibrium, while the Freundlich model has no equilibrium. The major difference between the Langmuir and Freundlich models is that one is homogeneous and the other is heterogeneous at the surface of the solid adsorbent. Moreover, Langmuir indicates mono molecular adsorption, while Freundlich is consistent with multi-molecular adsorption.

To analyze the isotherm of the Freundlich model, data including particle size of 1.18-2.36 mm, q_e (mg g^{-1}), C_e (mg L^{-1}), In q_e and In C_e are required. Then, the graph of In (q_e) vs In (C_e) is plotted, followed by the identification of the Freundlich parameters, K_F (mg g^{-1}), 1/n and R^2, as shown in Eq. 4.

$$\ln q_e = \ln K_F + {}^1\!/_n \ln C_e \qquad \textbf{Eq. 4}$$

To find the parameters, the following equation is used:

$$y = mx + c \qquad \textbf{Eq. 5}$$

where y stands for ln q_e, m stands for 1/n, x for In C_e, and c stands for K_F.

For the analysis of the Langmuir isotherm model, data including q_e (mg g^{-1}), C_e (mg L^{-1}), $1/q_e$ and $1/C_e$ for adsorbent with the particle size of 1.18–2.36 mm were obtained. After that, a graph with a linear line for $1/q_e$ and $1/C_e$ for solution KH_2PO_4. q_{max} (mg g^{-1}), K_L (mg g^{-1}) R^2 was plotted. **Eq. 4** was used to find the parameters. The linear form is shown in **Eq. 6.**

$${}^1\!/q_e = {}^1\!/_{K_L}\, q_{max} C_e + {}^1\!/q_{max} \qquad \textbf{Eq. 6}$$

RESULTS AND DISCUSSION

Physico-chemical Characteristics of Adsorbents

Four types of analyses were performed to assess the physico-chemical characteristics of duck eggshells before and after the nitrate analysis procedure: energy dispersive X-ray fluorescence (EDXRF), scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy.

Energy Dispersive X-Ray Fluorescence (EDXRF) Analysis

The EDXRF result shows the elements present in the raw duck eggshells before and after nitrate adsorption. From Table 1, the main element in raw duck eggshells was oxygen, O, with 57.82 % before adsorption and 61.65 % after nitrate adsorption. This implies that oxidative processes occurred during adsorption. The content of potassium increased from 0.23% to 0.32% after adsorption, while phosphorus also increased to 0.13% after adsorption. Thus, the raw duck eggshells could be used as a fertiliser [24].

Table 1. Elements present in the raw duck eggshells before and after adsorption.

Type of adsorbent (% weight)		
Element	**Before adsorption**	**After adsorption**
O	57.82	61.65
Ca	41.95	29.78
S	0	8.14
K	0.23	0.32
P	0	0.13
Total	100	100

Scanning Electron Microscopy (SEM) Analysis

Figure 1 shows the surface morphology of raw duck eggshells at 60×, 200× and 1000× magnification obtained by SEM. Figure 1(a), 1(b) and 1(c) depict the SEM micrographs of raw duck eggshells before adsorption. The many pores and fibres visible on the surface of the raw duck eggshells may increase nitrate adsorption efficiency. Meanwhile, Figure 1(d), (e) and (f) show the surface of the raw duck eggshells after nitrate adsorption. The porosity achieved, as shown by the amount of pores in the duck eggshells, is functional in the nitrate adsorption process from groundwater [25]. As shown in Figure 1 (f), the pores on the surface of the raw duck eggshells were smaller after nitrate adsorption compared to before the adsorption process, as in Figure 1 (c).

X-ray Diffraction (XRD) Analysis

Figure 2(a) shows that the predominant component in the raw duck eggshells was magnesium calcite, at 78 %. This increased to 80 % following nitrate removal, as shown in Figure 2(b). Aside from that, the raw duck eggshells contained calcite both before and after nitrate removal. After the adsorption process, the calcite content dropped from 22 % to 20 %. The reduction of calcite indicated the adsorption of nitrate into groundwater [26], and the removal efficiency was 49.3 %.

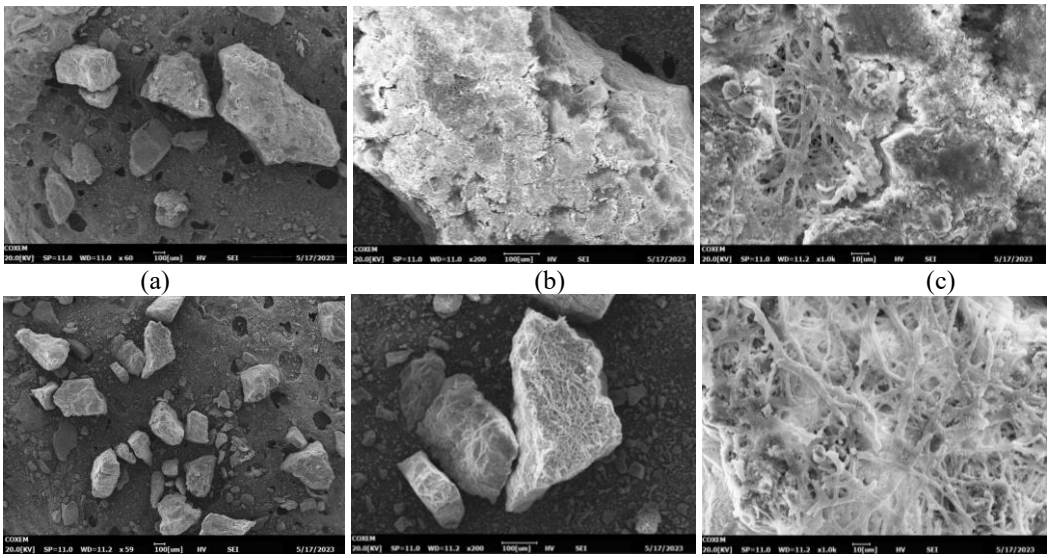
Fourier Transform Infrared (FTIR) Analysis

Fourier transform infrared (FTIR) analysis was carried out to identify the functional groups and vibrational bands involved in the nitrate adsorption process. The FTIR spectra of the raw duck eggshell samples before and after adsorption are presented in Figure 3, illustrating the differences in vibration types and frequencies of functional groups.

Table 2 shows that before adsorption, the major absorption peaks were observed at 3564.15 cm^{-1}, 2919.96 cm^{-1}, 2508.57 cm^{-1}, 1797.61 cm^{-1}, 1644.08 cm^{-1}, 1395.69 cm^{-1}, 871.96 cm^{-1}, and 711.77 cm^{-1}. After nitrate adsorption, these peaks shifted to 2086.03 cm^{-1}, 1791.25 cm^{-1}, 1741.97 cm^{-1}, 1396.17 cm^{-1}, 1085.66 cm^{-1}, 872.13 cm^{-1}, 711.93 cm^{-1}, and 679.81 cm^{-1}, respectively, indicating changes in surface chemistry due to nitrate interactions. Four functional groups, namely conjugated acid, carboxylate, carbonate ion, and aryl thioethers, were consistently detected before and after the adsorption process. For instance, the conjugated acid band shifted from 1797.61 cm^{-1} to 1791.25 cm^{-1}, showing a decrease of 6.31 cm^{-1}, while the carbonate ion band increased slightly, from 871.96 cm^{-1} to 872.13 cm^{-1}. These shifts suggest that chemical bonding and ion exchange occurred between nitrate ions and the functional groups on the eggshell surface. Overall, the spectral changes confirmed that nitrate molecules were successfully adsorbed onto the raw duck eggshells through interaction with surface carbonate and other active groups.

Adsorption Capacity and Removal Efficiency of Nitrate

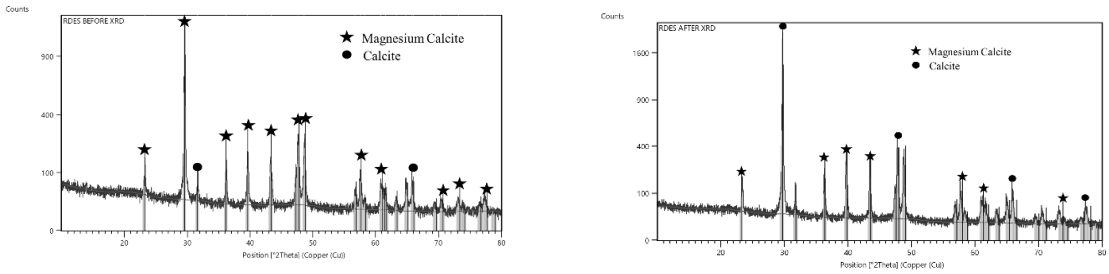
Figure 4(a) depicts the efficiency of nitrate removal based on the different masses of adsorbent (2, 4, 6, 8 and 10 g) and time (30, 120, 300, 1440, and 4320 min). Figure 4(a) shows that the nitrate removal efficiency was the highest at 49.3%, for 10 g of adsorbent and 4320 min. The removal of nitrate may be facilitated by the pores in the raw duck eggshells, which allow nitrate to adsorb easily, as shown in Figure 1(f). Raw duck eggshells also contain positive ions that can react with the negatively charged nitrate ions [27].



(a) (b) (c)

(d) (e) (f)

Figure 1. SEM photomicrographs (a) 60×, (b) 200×, (c) 1000× magnification before adsorption, and (d) 60×, (e) 200×, and (f) 1000× magnification after adsorption.

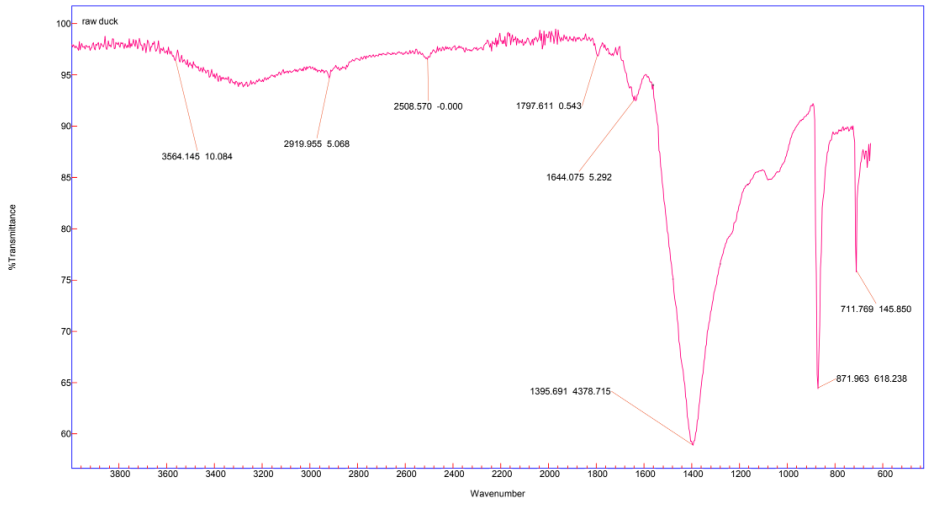


(a) (b)

Figure 2. XRD patterns and composition of raw duck eggshells (a) before, and (b) after the phosphorus adsorption process.

The adsorption capacity per unit mass, q_e indicates that the higher the adsorbent mass, the lower the adsorbing nitrate capacity. This is because a higher concentration of adsorbent causes the adsorption process to slow down, as shown in Figure 4(b) [28]. This is shown in Figure 1(f) where the pores on the duck eggshells surface were fewer and unclear compared to those in Figure 1 (c).

Although the removal efficiency increased with higher adsorbent mass, q_e showed the opposite trend. A maximum removal efficiency of 49.3 % was obtained at 10 g of adsorbent, while the highest adsorption capacity of 0.1200 mg/g occurred with 2 g of adsorbent. This inverse relationship can be explained by the effect of adsorbent dosage on the utilization of active sites. When a larger amount of adsorbent is introduced, more adsorption sites are available. However, the amount of nitrate ions in the solution remains constant. As a result, the available nitrate molecules are distributed among a greater number of active sites, leading to lower site utilization and, consequently, a reduced adsorption capacity per gram of adsorbent. In contrast, at lower adsorbent dosages, the ratio of nitrate ions to active sites is higher, resulting in greater surface coverage and a higher adsorption capacity. Therefore, while increasing adsorbent mass enhances overall nitrate removal from the solution (higher removal efficiency), it simultaneously decreases the adsorption capacity per unit mass due to unsaturated sites and particle aggregation at higher dosages [28].



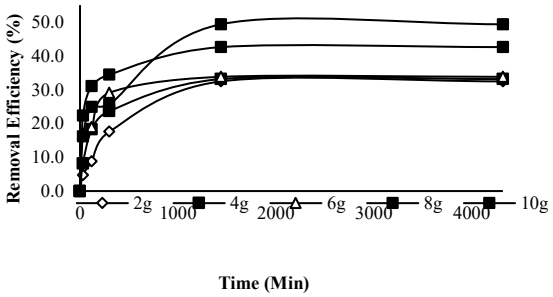
(a)

(b)

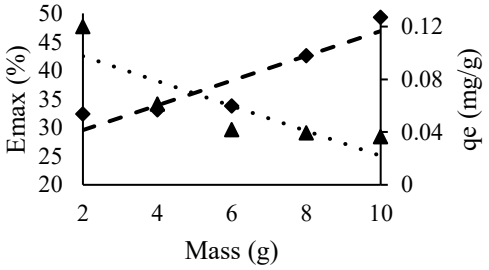
Figure 3. FTIR spectra of raw duck eggshells, (a) before, and (b) after adsorption of nitrate

Table 2. Functional groups in the FTIR spectra of raw duck eggshells before and after nitrate adsorption

Wavelength Frequency of the spectrum (cm^{-1})			Functional group class	Type of vibration	Reference
Before Adsorption	**After Adsorption**	**Differences**			
3564.15	-	-	Phenols	OH	[1]
-	2086.03	-	Isothiocyanate	–NCS	[1]
2919.96	-	-	Alkane	C–H	[1]
2508.57	-	-	Carboxylic acid	O-H	[2]
1797.61	1791.25	6.31	Conjugated acid halide	C=O	[1]
-	1741.97	-	Esters	C=O	[1]
1644.08	-	-	Open-chain imino	–C=N-	[1]
1395.69	1396.17	−0.48	Carboxylate	-	[1]
-	1085.66	-	Cyanate	–OCN and C–OCN	[1]
871.96	872.13	−0.17	Carbonate ion	-	[1]
711.77	711.93	−0.16	Aryl thioethers	C–S	[1]
-	679.81	-	Sulfate ion	-	[1]



(a)



(b)

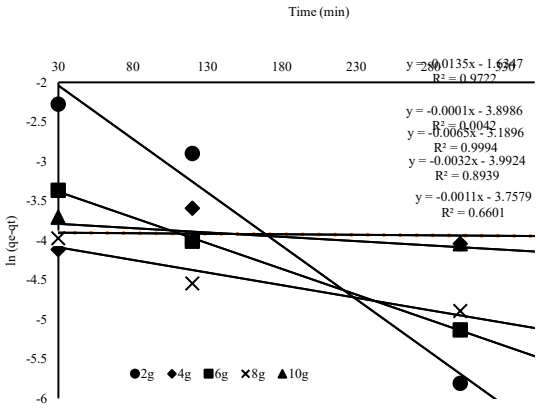
Figure 4. (a) Removal efficiency, E vs time; (b) Adsorption capacity, E_{max} and q_e vs mass.

Analysis of Kinetic Adsorption Models

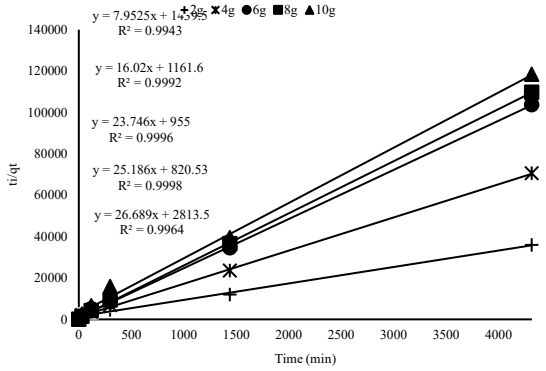
The pseudo first order (PFO) model's results in Table 3 were the best fit as it had the lowest value for F_e, 0.0492. In comparison, the pseudo second order (PSO) model's results in Table 4, gave an F_e value of 0.0854. The value of F_e can be calculated with Eq. 7. The best kinetic model is the one with the lowest F_e value [29].

$$F_e = \sqrt{\left(\frac{1}{n-p} * \sum_i^n (qt(\exp) - qt(theo)\right)^2} \quad \textbf{Eq. 7}$$

The PSO model resulted in a correlation coefficient R^2 of 0.9998, which was closer to 1 compared to the PFO model, which obtained an R^2 of 0.9994. As a result, PSO was the best fit kinetic model. This PSO model was consistent with the adsorption mechanism involved in the nitrate elimination process [30]. Figures 5(a) and 5(b) show that PSO had the closest linear correlation with the data.



(a)



(b)

Figure 5. (a) Pseudo-First Order kinetic model, (b) Pseudo-Second Order kinetic model.

Table 3. Kinetic parameters from the PFO model for the adsorption of raw duck eggshells.

Mass (g)	$q_{e(theo)}$ (mg/g)	k_1 (1/min)	R^2	F_e	$q_{e\ (exp)}$ (mg/g)
2	0.1950	0.0135	0.9722	0.2756	0.1200
4	0.0203	0.0001	0.0042	0.1436	0.0613
6	0.0412	0.0065	0.9994	0.0100	0.0417
8	0.0185	0.0032	0.8939	0.0722	0.0394
10	0.0233	0.0011	0.6601	0.0492	0.0365

Table 4. Kinetic parameters from the PSO model for the adsorption of raw duck eggshells.

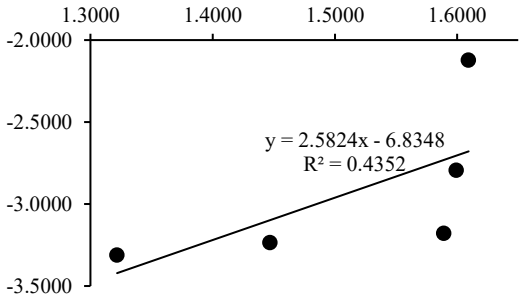
Mass (g)	$q_{e\ (theo)}$ (mg/g)	k_2 (g/mg/min)	R^2	F_e	$q_{e\ (exp)}$ (mg/g)
2	0.1257	0.0439	0.9943	0.2470	0.1200
4	0.0624	0.2209	0.9992	0.1501	0.0613
6	0.0421	0.5904	0.9996	0.1142	0.0417
8	0.0397	0.7731	0.9998	0.1119	0.0394
10	0.0375	0.2532	0.9964	0.0854	0.0365

Analysis of Isotherm Adsorption Models

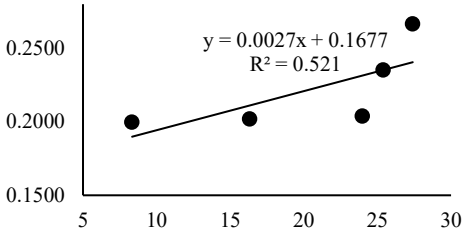
The isotherm model analysis results show that the Langmuir model was the best fit for the adsorption of nitrate in groundwater. The Langmuir model gave a correlation coefficient R^2 of 0.5210, which was closer to 1 compared to that of the Freundlich model, 0.4352 (Table 5). Furthermore, the adsorption capacity of the Langmuir Model, K_L, was higher than that of the Freundlich Model, K_F, indicating that the Langmuir model had the most suitable area and porosity of adsorbent, due to the pores on the surface of the raw duck eggshells, as in Figure 1(c) [31]. Figure 6 shows that the Langmuir Model (b) had the best fit line compared to the Freundlich Model (a), as the groundwater concentration was high. The Freundlich isotherm model distributes adsorption on the heterogeneous surface of the adsorbent, while the Langmuir isotherm model is the best fit for liquid based adsorption as our study was on the adsorption of nitrate in groundwater [32].

Table 5. Results of the Freundlich and Langmuir models.

Freundlich model			Langmuir model		
n	K_F (mg/)	R^2	q_{max} (mg/g)	K_L (L/mg)	R^2
5.9347	2.0066	0.4352	5.9630	62.1114	0.5210



(a)



(b)

Figure 6. Analysis of isotherms: (a) Freundlich model, and (b) Langmuir model.

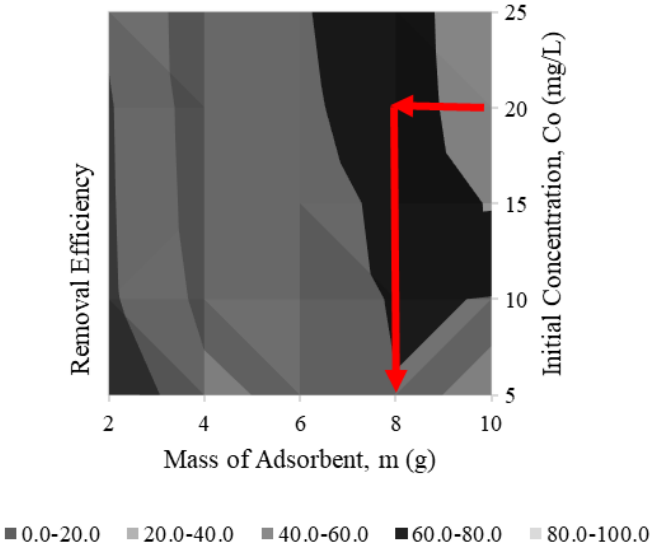


Figure 7. Contour prediction analysis.

Contour Prediction for Removal Efficiency

The prediction of nitrate removal efficiency may be made from the contour prediction, as shown in Figure 7 below. For example, there would be 60–80 % removal if 8 g of raw duck eggshells were used to remove nitrate in 20 mg/L of nitrate solution. With a solution containing 15 mg/L of nitrate, 6 g of raw duck eggshells could remove 40–60 % of the nitrate. Predictions are essential to estimate the amount of adsorbent needed and the removal efficiency with different initial concentrations.

CONCLUSION

In this study, kinetic and isotherm models were effectively implemented to clarify the mechanism of nitrate adsorption from synthetic solutions using raw duck eggshells as the adsorbent. The adsorption kinetics were best represented by the Pseudo-Second-Order (PSO) model (R^2 = 0.9167), suggesting that chemical adsorption governed the process. The Langmuir isotherm model (R^2 = 0.521) offered the closest linear model for the equilibrium data, indicating that adsorption occurred as a monolayer on a homogeneous surface. The highest adsorption capacity was 0.563 mg/g, while the highest nitrate removal efficiency reached 49.3 % using 10 g of adsorbent. These results demonstrate that raw duck eggshells are an effective and environmentally friendly material for removing nitrate from contaminated water. For future work, it is suggested to examine the regeneration and reusability of duck eggshell adsorbents, evaluate their efficiency in real groundwater systems, and explore surface modifications to further enhance their adsorption performance.

LIST OF ABBREVIATIONS

Abbreviation	Full Form / Description
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
PSO	Pseudo-Second-Order
PFO	Pseudo-First-Order
q_e	Equilibrium adsorption capacity (mg/g)
q_t	Adsorption capacity at time t (mg/g)
R^2	Correlation coefficient
F_e	Error function
KL	Langmuir adsorption constant (L/mg)
KF	Freundlich adsorption constant (mg/g)
q_{max}	Maximum adsorption capacity (mg/g)
NO_3^-	Nitrate ion
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
WHO	World Health Organization
EPA	Environmental Protection Agency

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