Removal of Nitrate from Aqueous Solution by Bio-Calcium from Iraqi Eggshells

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ABSTRACT

Nitrate contamination of drinking water is one of Iraq's environmental problems in some of its most vital lands as a result of sewage sedimentation, agricultural fertilizer waste, and remnants of war. Iraqi egg waste (bio-calcium Iraqi eggshells) was tested to remove nitrates, which is considered one of the best investments to achieve industrial sustainability on the one hand and reduce environmental problems on the other. The optimum conditions for removal were pH = 6, 120 min, 0.5 g Iraqi eggshells, and 150 rpm where 95.73% of nitrates were removed by Iraqi eggshells. The equilibrium data analysis determined that the (Langmuir isotherm) model was the best for describing adsorption, while (pseudo-second-order) adsorption kinetics were significantly appropriate for demonstrating nitrate adsorption kinetics, and a statistical model for nitrate removal percentage was developed.

Keywords: nitrate, aqueous solution, water treatment, eggshells, removal.

INTRODUCTION

Every year, a substantial quantity of eggshell trash is produced and wasted, resulting in a loss of natural resources and an environmental hazard. In this regard, eggshell waste reutilization has attracted significant interest. Where it is now considered one of the important ways to remove industrial and agricultural water pollutants, as well as the rest of the traditional methods of removal, such as ion exchange (Shang et al., 2022; Al-Agili, 2021), biological treatments (Masłoń & Czarnota, 2020), reverse osmosis (Ali, 2018), adsorption (Alshekhli et al., 2020), membrane separation (Ukhurebor et al., 2021), membrane separation (Zhang et al., 2019), catalysis (Teng et al., 2018). The global egg output in 2018 was estimated to be over 76 million tons (FAO, 2019). The eggshell contributes up to 11% of the egg's weight, resulting in 8 million tons of waste every year. One of the most intriguing aspects of eggshells is that they have numerous pores (7,000 to 17,000) and a pleasing appearance that can be used effectively (Guru & Dash, 2014). According

to a survey of the literature, both natural and physically or chemically modified eggshells have performed admirably in the removal of surfactants, heavy metals, and medicines, for example, chromium and cadmium ions interact with (carbonyl, hydroxyl, and carboxylic) functional groups that found in eggshells. Furthermore, Bismuth ions can be eliminated by pulverized chicken eggshells (Abbas et al., 2021). A high fixed carbon content and excellent performance for eliminating toluene and xylene pollutants were found under 60 minutes at pH = 10, biochar dosage of 2 g/L, and C_o = 40 mg/L for modified sewage sludge biochar by the eggshell (Kumi et al., 2022). When it comes to nitrates, they are among the most important of the most harmful ions to human health if their percentage exceeds the permissible limit which is (10 mg/L (NO_3-N)) in the US and (11.3 mg/L NO_3-N) according to WHO and Iraqi water laws (WHO, 2017; Iraqi, 2009). Looking at that, the groundwater used for drinking in Beibukht Khorsibat and Abbasiya was tested, which are located in Nineveh Governorate in Iraq, the results were 9.11–44.51 mg/l for nitrate concentration

which is considered higher than the allowable limit (Al-Gadi et al., 2023).

The study intends to employ eggshells from Iraqi sources as a low-cost adsorbent to remove nitrates from aqueous solutions, especially because the majority of research in Iraq is done at the researcher's expense. The influence of several parameters such as (pH, adsorbent mass, nitrate concentration, and contact time) was also examined in the laboratory. Isotherm and kinetic models were employed to validate the adsorption process. To forecast the removal ratio, a regression model associated with the variables (pH, nitrate concentration, agitation rate, and amount of adsorbent) was found along with theoretical findings using MINITAB-19 statistical software.

MATERIAL AND METHODS

Iraqi eggshells bio-calcium preparation

Eggshells (Iraqi products) were collected in batches from leftovers from home cooking, washed carefully with deionized water to remove liquid and solid plankton, then dried in the open air for 24 hours before being stored in an airtight container. These methods were repeated with all the collectives. The shells were then smashed with an electric grinder, and the crushed eggshells were filtered through laboratory sieves bearing record numbers into various sizes.

Bio-calcium components of the Iraqi eggshells were examined in Ibn-Sina laboratories. The results displayed that $CaCO_3$ is the most abundant with high porosity and a narrow particle size distribution as seen in Table 1, which

corresponded to many researchers who have provided papers on the components of eggshells in their countries such as Munira Khalid and others (Dervinytė, 2020; Khalid et al., 2022).

Influent solution

0.815 g of potassium nitrate (KNO3) were dissolved in 1000 ml deionized water and diluted in trials to 60, 70, 80, 90, 100, and 120 mg/l, the capacity of a 250 ml cup according to the equation (Jeremias et al. 2020):

$$V_o \times C_o = V_f \times C_f \tag{1}$$

where: V_o, V_f, C_o & C_f – initial and final volume and concentration respectively.

Analysis of laboratory and statistical data

The final nitrate concentrations were determined using a UV spectrophotometer with a wavelength of (215 nm), While MINITAB-19's Design of Experiment (DOE) statistical approach was utilized to accomplish optimal performance analysis, which compared input and output data to numerical data. A mathematical model shows the efficiency and capacity to remove nitrates.

Batch adsorption investigation

The batch test was carried out in a water bath using a magnetic stirrer and varied amounts of eggshells. The following equation was used to compute nitrate removal efficiency (Al-Agili, 2021):

$$R\% = \left[\frac{C_o - C_e}{C_o}\right] \times 100\% \tag{2}$$

Table 1. Components of the iraqi eggshells and laboratory figure

$CaCO_3$	97.24%	
$MgCO_3$	1.907%	
K_2CO_3	0.037%	

Using mass balance, the following equation was used to calculate the quantity of Nitrate adsorbed per unit mass of eggshells:

$$q_e = \frac{(C_0 - C_e) \times v}{w} \quad (3)$$

where: $R\%$ – the percentage of nitrate removed;
C_o and C_e – the starting and final concentrations of nitrate (mg/L);
q_e – the adsorption capacity;
V – the volume of solution (L);
W – the weight of eggshells (g).

Adsorption isotherm and kinetic studies

The maximum capacity of adsorption was calculated using the Langmuir isotherm model, while the Freundlich isotherm was utilized to explain the equilibrium between solid and solution as equations (Matsuska, 2020):
Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{c_e}\frac{1}{k_a q_m} \quad (4)$$

Freundlich equation:

$$\log q_e = \log k_f + \left(\frac{1}{n}\right)\log c_e \quad (5)$$

where: q_e – the equilibrium adsorption capacity (mg/g);
q_m – the full monolayer adsorption capacity (mg/g);
k_a – the adsorption equilibrium constant (L/mg);
c_e – nitrate at an equilibrium concentration (mg/L);
n and k_F – Freundlich constants.

In Kinetic Studies, Pseudo-first order and pseudo-second order kinetic equations were used to calculate the quantity of nitrate adsorbed over time (Matsuska, 2020; Igwegbe, 2019).
Pseudo-first order kinetic equation:

$$\ln(q_e - q_t) = \ln q_e + k_1 t \quad (6)$$

Pseudo-second order kinetic equation:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (7)$$

where: q_t and q_e are the adsorption capabilities at t time in minutes and equilibrium, respectively;
k_L and k – the pseudo 1st and 2nd order models' rate constants, respectively.

RESULTS AND DISCUSSION

Effect of pH on nitrate adsorption

The effect of pH change on nitrate removal was investigated in ranges 5, 6, 7, and 8 under 60 ppm concentration, 0.05 g eggshells amount, 50 rpm, and 15 min time stabilization. Hydrochloric acid (HCL) and Sodium hydroxide (NaOH) were utilized for pH adjusting. The generated adsorption increased steadily and gradually when the pH was raised until it reached pH = 6. The adsorption of Nitrate ions increases and the effectiveness of H^+ adsorption improves at pH = 6, the efficiency was 23.61% as shown in Figure 1. This is due to the increased amount of OH. At low pH, hydrogen ions cling to the adsorbent surface, reducing the number of adsorption sites and lowering the nitrate adsorption capacity. Furthermore, higher pH increases the strength of electrostatic repulsion between Ca^{+2} and nitrate at eggshells, delaying diffusion and absorption.

Determination of the equilibrium time for the adsorption of nitrate ions by the absorbent material

At 120 minutes, the efficiency rate was 52.68% under (60 ppm concentration, 0.05 g eggshells amount, 50 rpm, and PH calculated previously). Where the effect of equilibrium time was determined by 15, 30, 60, 90, 120, and 150 min. The percentage removal of nitrate is found to increase rapidly with time up to 120 minutes before becoming roughly constant by balancing the solid and liquid phases and filling the pores with nitrates, so 120 minutes were judged to be the best time for nitrate removal, as shown in Figure 2.
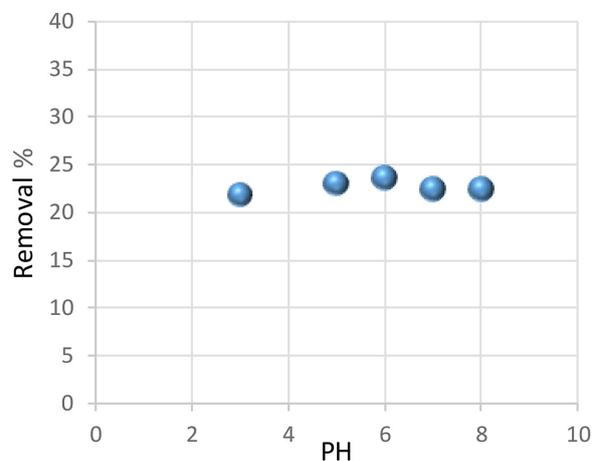
Figure 1. Effect of pH on nitrate adsorption
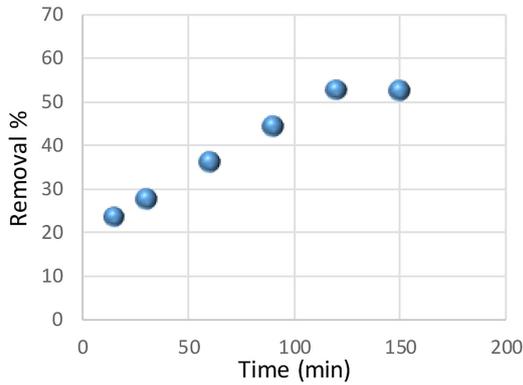
Figure 2. The equilibrium time for the adsorption of nitrate ions by the absorbent material
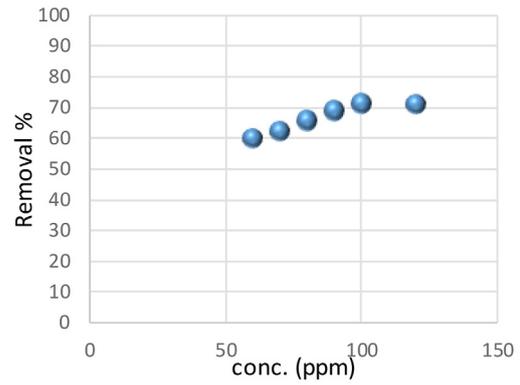
Figure 4. Effect of initial concentration on nitrate adsorption

Effect of Iraqi eggshells amount on nitrate adsorption

The influence of eggshells quantity was tested by immersing 0.05, 0.1, 0.3, 0.5, 1, 2, and 3 g of eggshells in 100 ml of a nitrate solution (60 ppm conc., 50 rpm, PH, and time calculated previously). Figure 3 illustrates how increasing the amount of eggshells adsorbent increases the effectiveness and capacity of nitrate ion adsorption.

The nitrate adsorption efficiency increased to 59.88% at the 0.5 g eggshells amount. As a result, the mass was set at 0.5 g.

Effect of initial concentration on adsorption

The influence of the initial nitrate content at 60, 70, 80, 90, 100, and 120 ppm on the optimal pH, time, and eggshells amount which were previously estimated using 50 rpm was
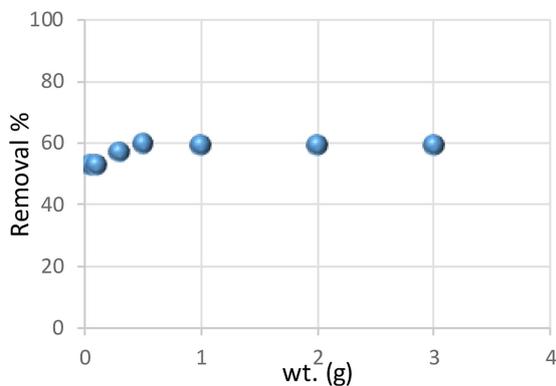
Figure 3. Effect of Iraqi eggshells amount on nitrate adsorption
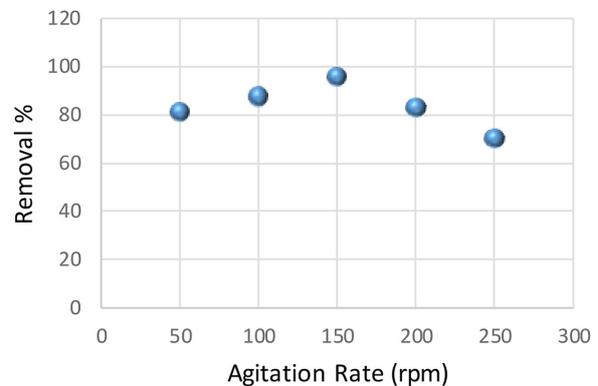
Figure 5. Effect of agitation rate on nitrate adsorption
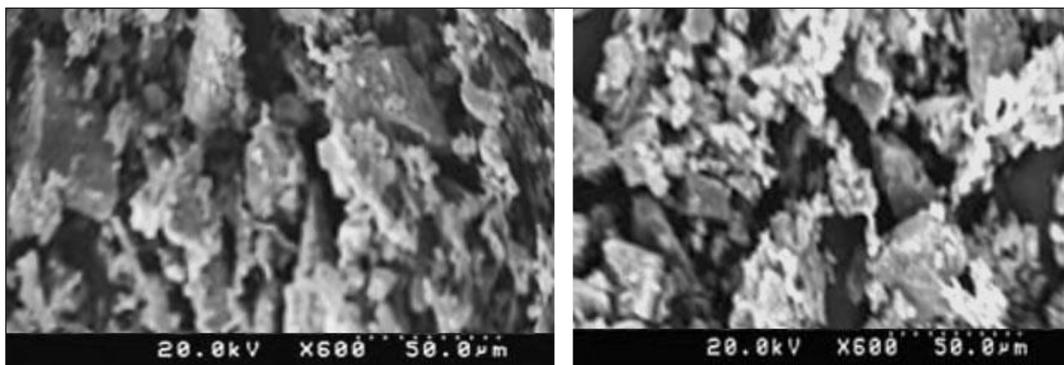
Figure 6. (a) SEM for Eggshell bio-calcium before nitrate removal, (b) SEM for Eggshell bio-calcium after nitrate removal

investigated as shown in Figure 4. The highest adsorption may take place at low concentrations because of the existence of the most active bands on the surface of the adsorbent, as well as an increase in the velocity of the mass transfer.

Effect of agitation rate on adsorption

The effect of the agitation rate was tested for 120 min using a water bath stirring shaker at 50, 100, 150, 200, and 250 rpm and optimum pH, con., eggshells amounts. Until 500 rpm, nitrate
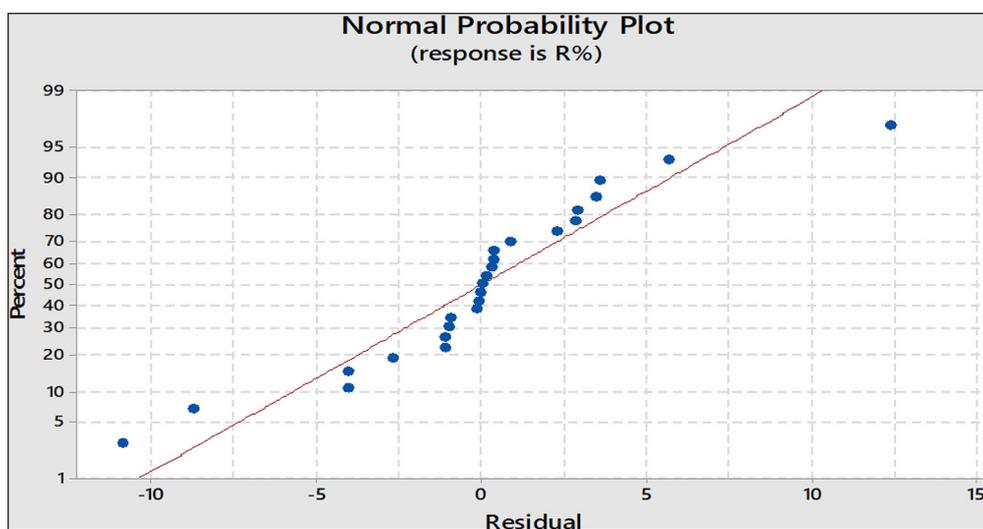
Figure 7. The normal distribution probability of nitrate removal percent

Table 2. Calculated values of Freundlich and Langmuir constants for nitrate adsorption over eggshells

Freundlich isotherm	Slope	Intercept	$1/n$	k_f	R^2
	4.25902	-4.89049	4.25902	1.2868E-05	0.92318
Langmuir isotherm	Slope	Intercept	q_m	k_l	R^2
	7.05512	-0.19687	-5.079494082	-0.027904557	0.96001
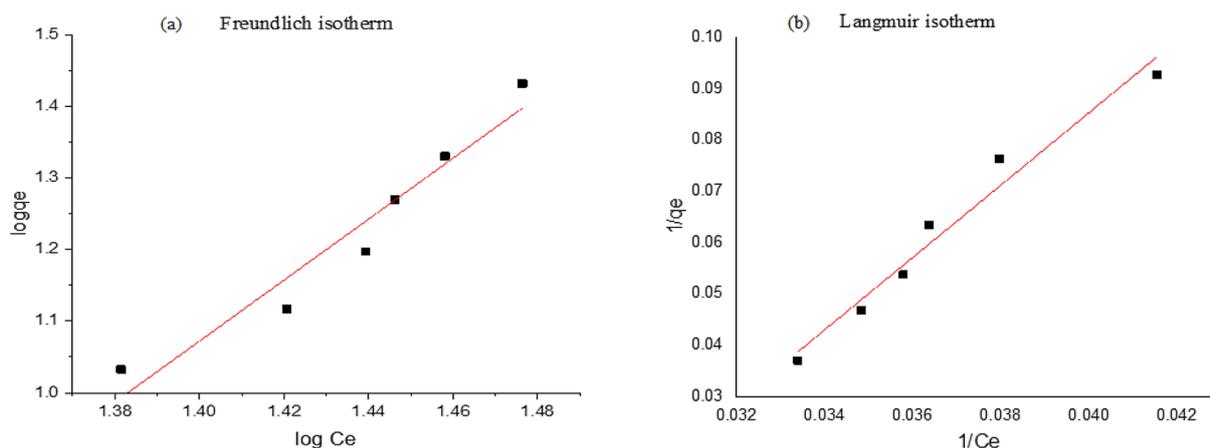
Figure 8. Freundlich and Langmuir adsorption isotherm for the nitrate removal

Table 3. Summary of pseudo-first-order and pseudo-second-order reversible reaction constant

Pseudo-first-order adsorption kinetic	Slope	Intercept	q_e	k_1	R^2
	-0.04458	5.19227	179.8764	-0.00037	0.78183
Pseudo-second-order adsorption kinetic	Slope	Intercept	q_e	k_2	R^2
	0.00869	0.26098	115.0748	0.000289	0.96705
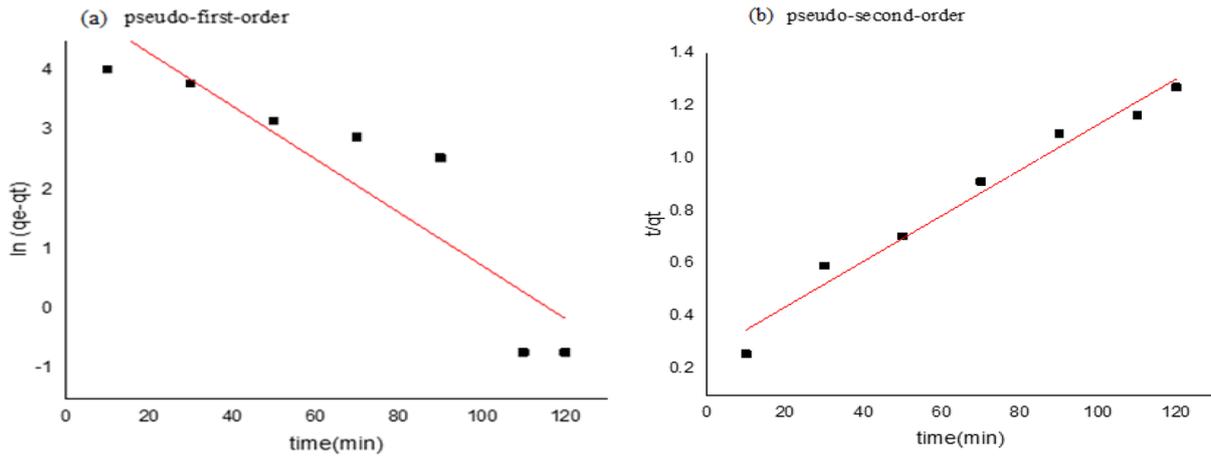
Figure 9. kinetic models for the adsorption of nitrate onto eggshells
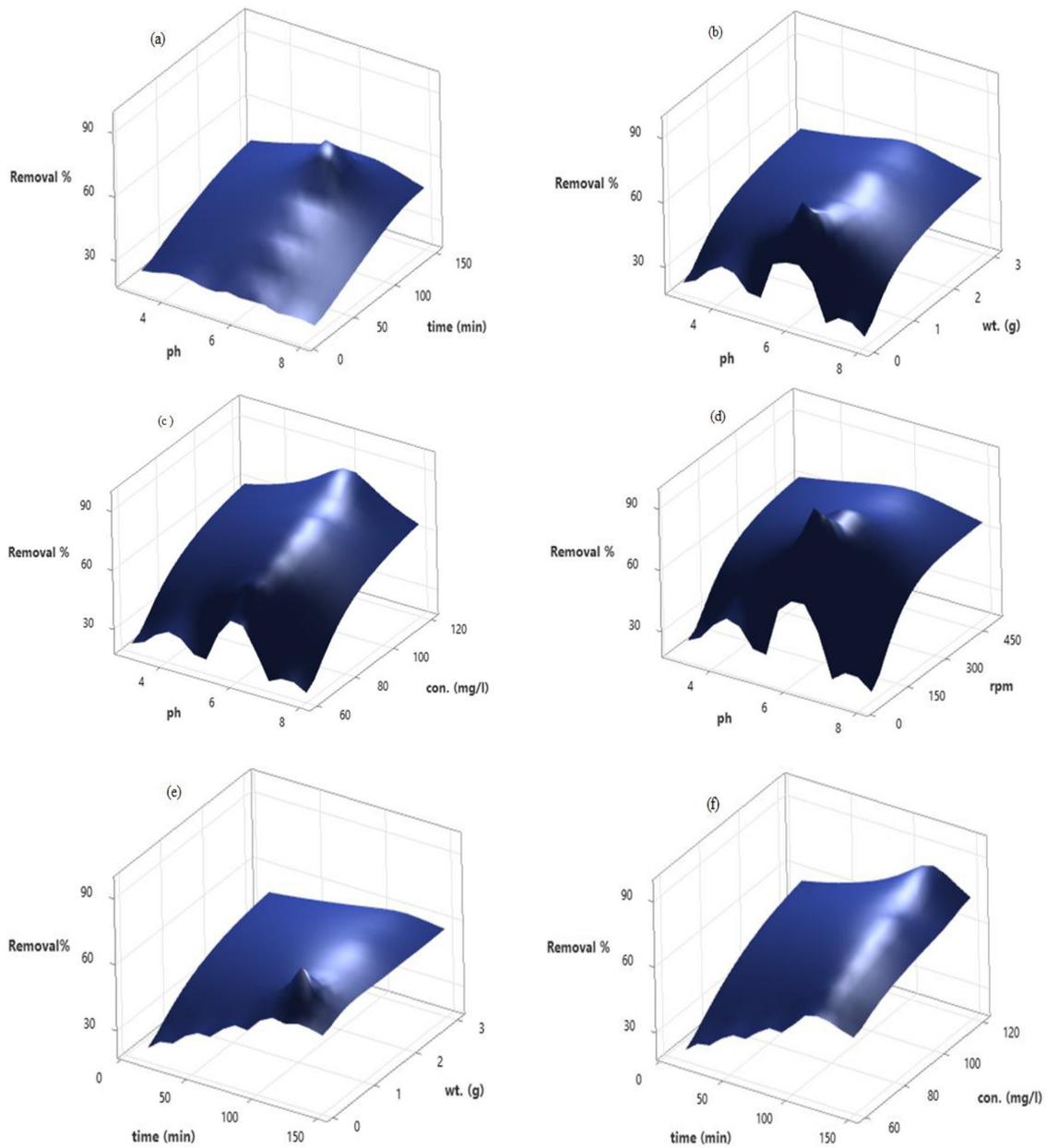
Figure 10. 3D response surface results for: (a) ph vs. Time (min), (b) pH vs. wt. (g),
(c) pH vs. con. (ppm), (d) pH vs. rpm, (e) time vs. wt.(g), (f) time vs. conc.
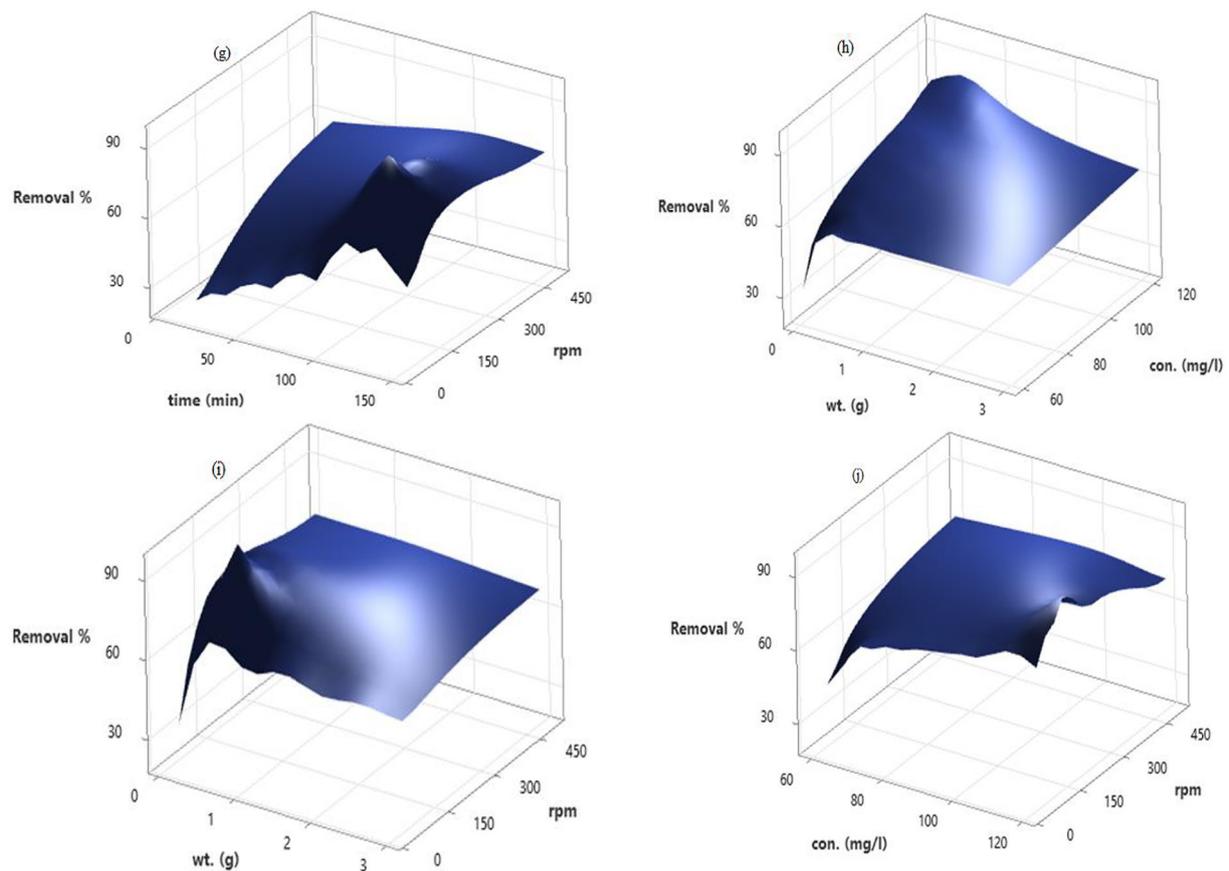
Figure 10. Cont. 3D response surface results for: (g) time vs. rpm,
(h) wt. vs. con. (mg/l), (i) wt. vs. rpm, (j) con. vs. rpm

adsorption and agitation rate were directly related, suggesting a proper interchange of solution and sorbent binding sites. Due to ionic attraction, removal efficacy is diminished over 150 rpm, as shown in Figure 5 and Figure 6.

Prediction of isotherms model

The MINITAB-19 statistical program was used to create a regression model, and the results were compared to theoretical values. Based on 25 runs of experiments, the following nitrate removal percent regression model was developed:

$$R\% = -12.38 + 0.14\,ph + 0.2818\,t + \\ +3.04\,wt. + 0.5288\,con. - 0.0258\,rpm \quad (8)$$

The regression model's (R-sq.) score is 95.81%. The model's fit to the data is represented by this number. As the value of R-sq climbed, the model suited the data better and the predicted responses were more reliable. Figure 7 illustrates the normal distribution probability of nitrate removal percent.

Equilibrium isotherm models

For in vitro data to better comprehend the mechanism of ion adsorption by the examined adsorbents, Freundlich and Langmuir isothermal models were investigated. Table 2 and Figure 8 both show that the Langmuir model fits more accurately than the Freundlich model.

Kinetic studies

The varying initial concentrations via pseudo-first-order and pseudo-second-order models are shown in Table 3. According to the findings, eggshells fit pseudo-second-order better than first-order, as seen in Figure 9. The response surface results are illustrated in Figure 10.

CONCLUSIONS

The results presented demonstrated that bio-calcium Iraqi Eggshells have a high potential as a nitrate adsorbent in water. Adsorption is

conditional on several variables, including the solution's pH, the duration of the adsorption process, the amount of eggshells, the concentration of nitrate, and the velocity of mixing. Optimal removal can be achieved at pH = 6, which is easily maintained and converted back to drinkable pH after nitrate removal treatment. The best nitrate removal percent was achieved for a time of 120 minutes, and the best amount of eggshell bio-calcium sorbent for the study conditions was 0.5 g. Iraqi Eggshells proved their ability to adsorb nitrates in different concentrations until it reaches the stage of surface saturation, where the removal rate becomes almost constant. The agitation rate had an important effect on the removal of nitrate because it controls the ionic attraction force, which affects the exchange adsorption binding sites. According to the study conditions, the best agitation rate was 150 rpm achieving 95.73 % which was the optimum removal of nitrates by eggshells. For the proportion of nitrate removal, a statistical model was developed. It showed a removal ratio of 95.81%, which is very similar to the removal percentage found in the lab. According to the examination of the equilibrium data, the Langmuir isotherm model best describes adsorption and pseudo-second-order adsorption kinetics substantially better illustrates how nitrate adsorbs to the surface of the adsorbent. The results were near to those by (Kugarajah et al., 2022) in comparing the performance of Microbial fuel cell biocathodes with and without eggshells which showed that eggshells had a superior performance with 97% nitrate removal and (Xu et al., 2016) who achieved 97% of removal Nitrate in synthetic groundwater by a sulfur-based autotrophic denitrification process utilizing eggshell.

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