Removing nitrate from contaminated water using activated carbon prepared from hard pistachio shells

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Abstract

Background: Currently, due to the scarcity of water resources and the water shortage crisis, the preservation of contamination of water resources is of particular importance. Nitrate is one of the most hazardous pollutants in aquatic environments, which leads to many health and environmental problems. Thus, finding environmentally friendly solutions to remove nitrate from water sources is essential. This study examined hard pistachio shells as a raw material for the preparation of activated carbon and their use as an adsorbent.

Materials and Methods: The experimental laboratory study explored factors affecting the absorption process including initial nitrate concentration, pH, absorption dosage, and reaction time on nitrate removal efficiency. The structural properties of the adsorbent were investigated by field emission scanning electron microscopy and the point of zero charge (pH_{pzc}). Finally, the adsorption kinetics and isotherms were investigated.

Results: Under optimize conditions, including initial nitrate concentration of 50 mg/L, adsorbent dosage of 0.2 g/L, pH equal to 5, and reaction time of 30 min, activated carbon can remove 99.4% of nitrate. The maximum adsorbent capacity was 211.6 mg/g. Nitrate removal follows quadratic kinetics and the Langmuir isotherm.

Conclusion: The surface adsorption process using activated carbon prepared from hard pistachio shells can lead to the effective management of pistachio shells and has a significant efficiency in the removal of nitrates with high concentrations.

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1. Introduction

Limited water resources and the risk of a water crisis in the country, on the one hand, and the increase in surface and groundwater pollution by pollutants from municipal and industrial wastewater, on the other hand, have caused major health and economic concerns. To this end, many efforts have been taken to find effective and eco-friendly solutions to remove pollutants from water sources. Nitrate is one of the important pollutants of surface and groundwater resources that enter water resources through raw human, industrial and agricultural wastewaters. The presence of nitrate in water sources caused many problems and diseases, including increased neonatal mortality, the risk of miscarriage, methemoglobinemia in children, the formation of carcinogenic nitrosamines in adults, and other diseases [1, 2]. Besides, the presence of nitrate in water causes etherification of water resources, loss of fish and aquatic organisms, dysfunction of photosynthesis of aquatic plants, and related problems [3, 4]. There are various physical, chemical, and biological methods used to remove contaminants, including filtration, adsorption, activated sludge, membrane bioreactors, ion exchange, etc. [5-7]. Chemical treatment systems have relatively high operating costs and the problem of sludge disposal during the treatment process. Besides, in some cases, by-products produced by these systems are more dangerous than the primary contaminant. Furthermore, biological methods require great care and organic substrate and produce a huge amount of sludge and thus need to be equipped with sludge management and treatment and disposal facilities [8, 9].

One of the water and wastewater treatment methods is the surface adsorption method using various adsorbents. Despite the need for an efficient adsorbent, this method has a special priority in water and wastewater treatment due to its cost-effectiveness, easy operation, low use of chemicals and eco-friendly processes, and good efficiency in water and wastewater treatment [10, 11]. Activated carbon is widely used as a surface adsorbent in the removal of water and wastewater contaminants due to its high surface-to-volume ratio, small pore diameter, and high chemical stability in acidic and alkaline environments.

Recently research has shown that the function of activated carbon in the removal of pollutants, in addition to the tissue properties and pore structure, depends on the type of raw material and the method of activation. Another point to note is that there are many pistachio gardens in Iran, especially the city of Rafsanjan that produce a large volume of pistachios. After consuming pistachios, the hard shells were discarded and left unused. These wastes are mainly consumed either as fuel or buried, which causes serious damage to the environment; This being so, the present study aims to explore the possibility of using pistachio waste (hard pistachio shells) as a raw material to make activated carbon and use it to remove nitrate from water resources. It also examines the effect of various parameters such as initial nitrate concentration, solution pH, adsorbent dosage, and reaction time, and adsorption kinetics and isotherms.

2. Materials and Methods

Absorbent preparation

To produce activated carbon, hard pistachio shells were collected, crushed, and washed several times with distilled water, and dried at 100±5 °C. In the next step, they were mixed with phosphoric acid at a concentration of 95% and a weight percentage of 1 to 100 (1 g shell-100 mL of phosphoric acid). After filtering, the sample was placed in a furnace at 900 °C for 1 hour. The produced carbon was rinsed with distilled water to neutralize its pH. The final product was heated for one hour at 100±5 °C to dry and finally meshed with a standard sieve and used as an adsorbent to remove nitrate.

Absorption tests

Adsorption tests were performed discontinuously at room temperature using 250-mL Pyrex containers. The adsorption process was performed by mixing different amounts of nitrate in the range of 25-100 mg/L, adsorbent values in the range of 0.05-0.3 g/L, pH of the solution in the range of 3 to 11 at intervals of 5 to 60 minutes. The pH of the samples was measured and adjusted with hydrochloric acid and sodium hydroxide by a pH meter. Upon the completion of the reaction, the samples were centrifuged and then measured using a UV/Vis spectrophotometer (Shimadzu-1700, Japan) at a wavelength of 272 nm. The optimization process was evaluated at each step by changing only one variable, and keeping the other variables constant. To ensure the reproducibility of the data, each experiment was repeated three times and the average results were reported.

Adsorption isotherm and kinetics

At equilibrium, there are constraints on the distribution of pollutants between liquid and solid phases, which are explained by several isotherm models. Two widely used equations to describe adsorption isotherms in solid and liquid systems are the Langmuir and Freundlich equations. According to Langmuir's theory, adsorption occurs at a specific homogeneous location in the adsorbent orifice. Freundlich isotherm is an experimental equation mostly used to understand the adsorption of contaminants on a heterogeneous surface by multilayer adsorption. Table 1 shows the Langmuir and Freundlich isotherm equations [12]:

Table 1: Langmuir and Freundlich isotherm equations

Isotherms	Isotherm equations	Parameters
Langmuir	$\frac{Ce}{qe} = \frac{1}{bqm} + \frac{Ce}{qm}$	q_e: Equilibrium absorption capacity (mg/g) q_m: Maximum absorption capacity (mg/g) C_e: Pollutant concentration after adsorption (mg/L) b: Langmuir constant
Freundlich	$\ln q_e = \ln k_f + \frac{1}{n} \, lnC_e$	C_e: Pollutant concentration after adsorption (mg/L) q_e: Equilibrium absorption capacity (mg/g) K_f, n: Freundlich constants

Adsorption kinetics explains the relationship between the chemical and physical properties of the adsorbent, the adsorbed material particles, the effect of the adsorption mechanism, and the reaction paths during equilibrium times. Most kinetic models for surface adsorption are first and second-order models. In first-order models, the rate of reaction is proportional to the concentration of the reactant. Table 2 presents the first and second-order kinetic equations and the corresponding parameters [12]:

Table 2: The first and second-order kinetic equations

Kinetics	Kinetic equations	Parameters
First order	$\log(q_e - q_t) = \log(q_e) - k_1 t/2.303$	q_t: Absorption capacity (mg/g) at time t q_e: Equilibrium absorption capacity (mg/g) K_1: First-order kinetic constant (min^{-1})
Second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	q_e: Equilibrium absorption capacity (mg/g) K_1: Second-order kinetic constant (min^{-1})

3. Results

Absorbent surface profile

Figure 1 shows the images from the FE-SEM analysis of activated carbon obtained from hard pistachio shells:

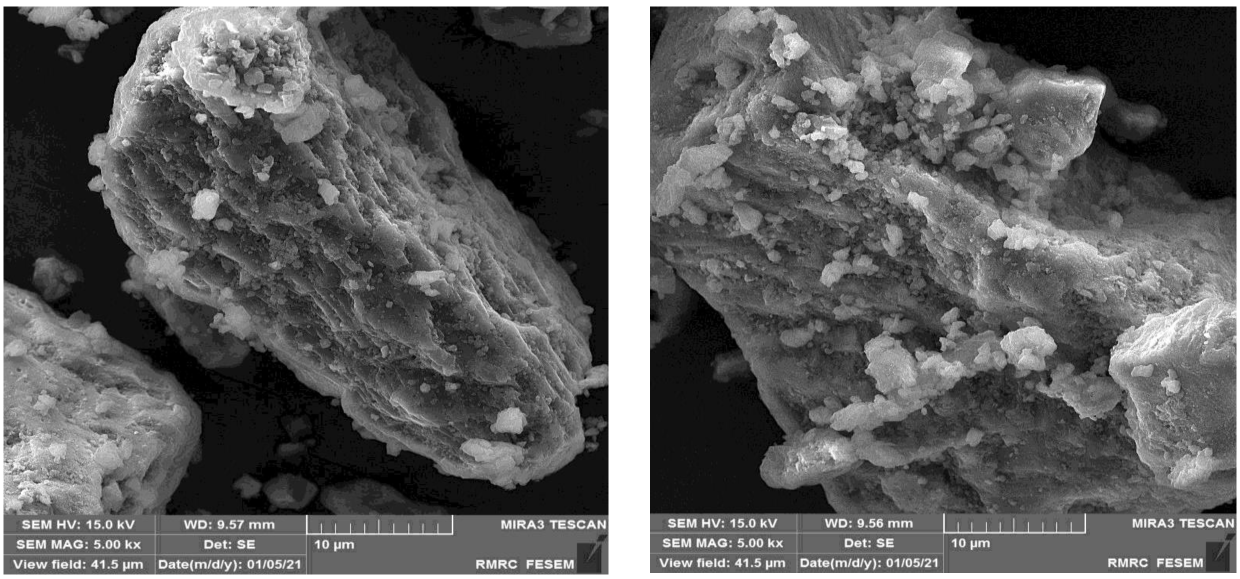

Figure 1: Field Emission Scanning Electron Microscope (FE-SEM) images of activated carbon prepared from hard pistachio shells

The effect of nitrate concentration on removal efficiency

To determine the effect of initial nitrate concentration on the rate of removal by activated carbon from pistachio shells, initial concentrations of 25, 50, 75, and 100 mg/L nitrate were analyzed. The experiments at this stage were performed at pH of 7, activated carbon of 0.15 g/L, and contact time of 60 min. The results were calculated in terms of the percentage of removal efficiency, as shown in Figure 2:

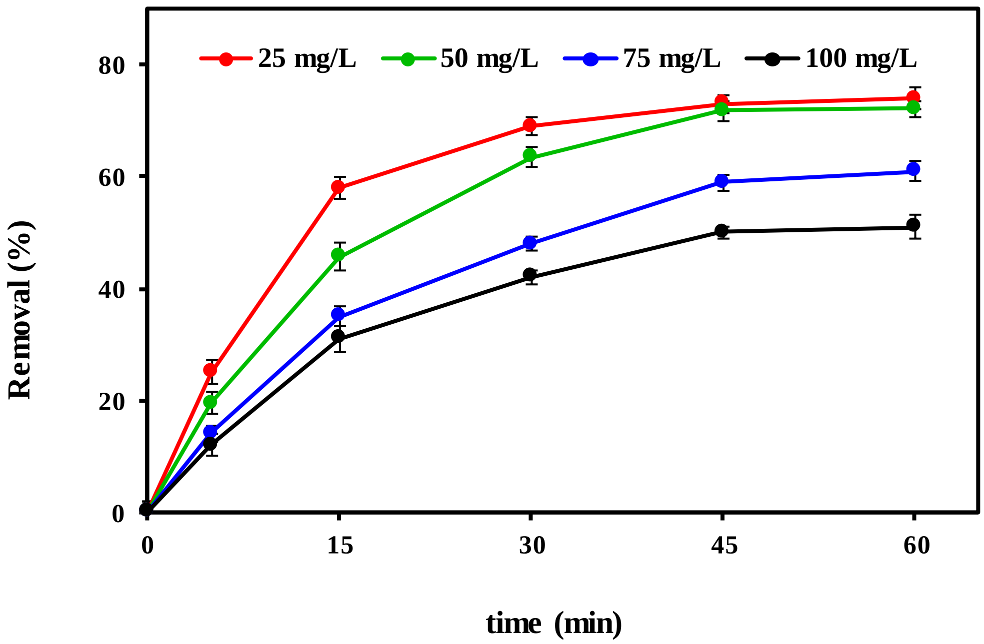

Figure 2: The effect of initial nitrate concentrations on removal efficiency of activated carbon

As shown in Figure 2, the highest removal efficiency rates, i.e. 74.3% and 72.1%, were observed at concentrations of 25 and 50 mg/L, respectively. The lowest removal efficiency (51.7%) was observed in the initial concentration of 100 mg/L. Accordingly, as the removal efficiencies were almost the same at concentrations of 25 and 50 mg/L; thus, the concentration of 50 mg/L was selected as the optimal concentration.

The effect of solution pH on nitrate removal efficiency

To determine the effect of pH on nitrate removal by activated carbon prepared from pistachio shells, pH values of 3, 5, 7, 9, and 11 were analyzed. For each experiment, 0.15 g/L of activated carbon was added to the reactor containing nitrate with a constant concentration of 50 mg/L. Besides, sampling was performed at times 0 to 60 min and the residual nitrate was measured. The removal efficiency percentages for different pH values are shown in Figure 3:

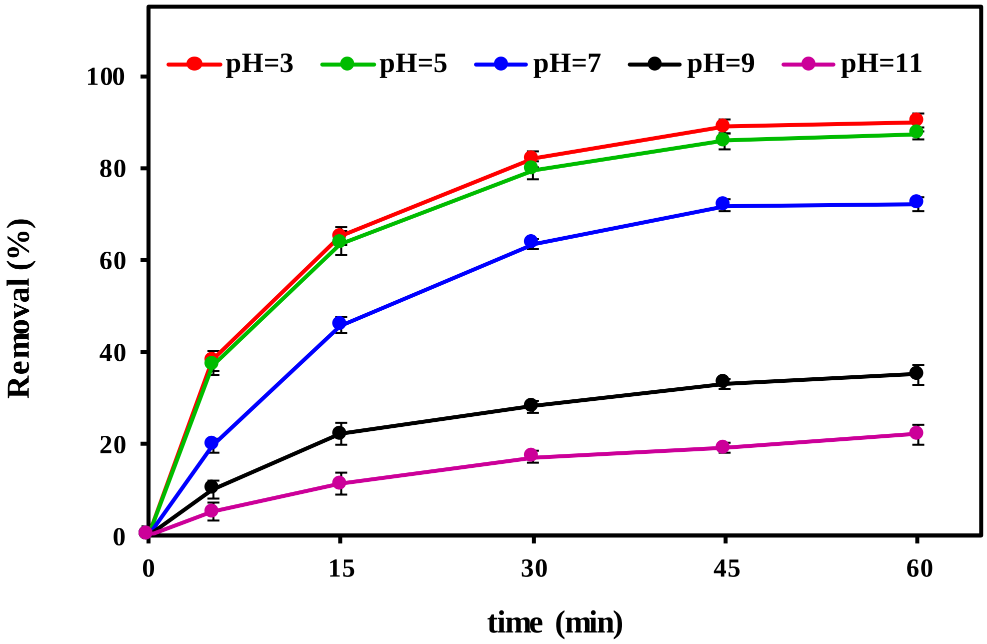

Figure 3: The effect of solution pH on the removal efficiency of nitrate by activated carbon (nitrate concentration: 50 mg/L, and activated carbon: 0.15 g/L)

As can be seen in Figure 3, the highest removal efficiency rates, i.e. 90.3% and 88.7%, were observed at the pH values of 3 and 5, respectively. The lowest removal efficiency rates (53.3% and 22.8%) were also observed at the pH values of 9 and 11, respectively. Accordingly, as the removal efficiencies were almost similar to the pH values of 3 and 5, thus the pH equal to 5 was selected as the optimal pH due to its proximity to the neutral pH.

The effect of the amount of activated carbon on nitrate removal

To determine the effect of the amount of activated carbon on the nitrate removal efficiency, different values of 0.05, 0.1, 0.15, 0.2, and 0.3 g/L of activated carbon were analyzed. For each experiment, 50 mg/L nitrates and a pH of 5 were considered. Besides, activated carbon at the mentioned concentration was added to the reactor at contact times 0 to 60 min. The removal efficiency percentages for different values of activated carbon are shown in Figure 4:

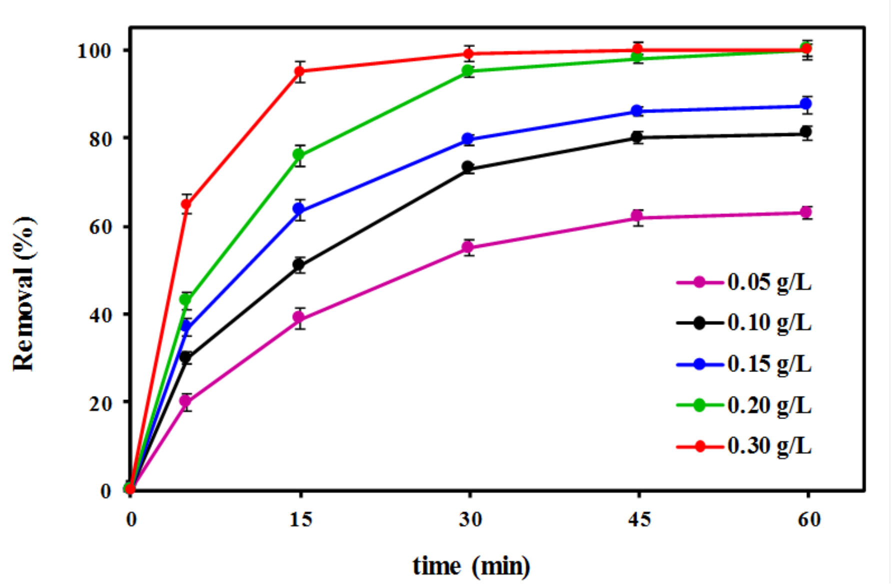

Figure 4: The effect of different values of activated carbon on the nitrate removal efficiency (nitrate concentration of 50 mg/L and pHof 5)

As shown in Figure 4, the highest removal efficiency rates, i.e. 99.4% and 99.9%, were observed at the concentrations of 0.2 and 0.3 g/L, respectively. The lowest removal efficiency (63.1%) was observed in the absorbent concentration of 0.5 g/L. Accordingly, as the removal efficiencies were almost the same at the concentrations of 0.2 and 0.3 g/L; thus, the concentration of 0.2 g/L was selected as the optimal concentration.

To determine the effect of contact time, the absorption experiments were conducted at the contact times of 5, 15, 30, 45, and 60 min. For each experiment, 0.2 g/L of adsorbent, nitrate with a constant concentration of 50 mg/L, and a pH of 5 were considered. The experiments were conducted at different contact times and the nitrate residual values were measured. The results indicated that the removal efficiency reached equilibrium in 30 min, so 30 minu was selected as the optimal time.

Isotherm and kinetics

As mentioned, the two equations widely used to describe adsorption isotherms in the solid-liquid system are the Langmuir and Freundlich equations. The vales of the Langmuir and Freundlich isotherms and correlation coefficients are presented in Table 3:

Table 3: The values of adsorption isotherms and correlation coefficients

Isotherms						
Langmuir				Freundlich		
R_L	q_m (mg/g)	b (L/mg)	R^2	K_f (L/g)	n	R^2
0.056	211.6	1.23	0.9983	65.4	3.11	0.9156

As can be seen in Table 3, the value of n in the Freundlich isotherm was 3.11 and the value of K_f was 65.4 L/g. Besides, q_m equal to 211.6 mg/g.

The values for the first and second-order kinetic parameters of the adsorption process and the correlation coefficients are presented in Table 4. As can be seen, the correlation coefficient for the quadratic kinetic model is higher than that of the quadratic kinetic model.

Table 4: The numerical values for the kinetic parameters of the adsorption process

Kinetic parameters					
First-order			**Second-order**		
qe (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g.min/mg)	R^2
186.3	0.0015	0.9249	161.2	0.0032	0.9963

As shown in Table 4, the values of q_e or equilibrium adsorption capacity (mg adsorbed per gram of adsorbent in equilibrium) in the first-order and second-order kinetics were 186.3 mg/g and 161.2 mg/g, respectively.

4. Discussion

As displayed in the electron microscope images, the activated carbon produced from hard pistachio shells has a rough surface with a porous and nested structure. The reason for the porosity in the structure of the absorbent is the presence of lignin and cellulose in the structure of the raw material used to produce activated carbon. The porous structure of the adsorbent increases the adsorption capacity and this correspondingly increases the efficiency of the adsorbent in the surface adsorption process of contaminants.

The assessment of the parameters affecting the adsorption process showed that one of the most important factors affecting the adsorption process is the initial concentration of contaminants (nitrate). In this study, the initial concentration of nitrate was analyzed in the range of 25 to 100 mg/L to show its removal efficiency. The results showed that increasing the initial concentration of nitrate negatively affects removal efficiency. By increasing the nitrate concentration from 25 to 100 mg/L, the removal efficiency decreases from 74% to 51%. Besides, increasing the initial concentration of the contaminant and its effect on reducing the efficiency of the removal process has also been demonstrated in other studies. To account for the declining trend of removal efficiency with increasing initial concentration, it can be argued that in a constant amount of adsorbent, the active adsorption sites are constant. However, with increasing concentrations of the adsorbent (contaminant), the number of contaminant molecules in the reaction medium increases [13, 14].

pH is one of the most important parameters affecting the adsorption process. In this study, pH varied in the range of 3 to 11 and its effect on nitrate removal efficiency was assessed using the adsorption process. According to the results, pH negatively affects nitrate removal efficiency in the adsorption process. In other words, increasing pH decreases the removal efficiency. The maximum nitrate removal efficiency was obtained at a pH of 0.5.

In the surface adsorption process, the ionic form of the contaminant molecule, the pHzpc of the adsorbent, and the functional groups present on the adsorbent surface play the most important role in the adsorption process. At acidic pH, nitrate removal efficiency is high and decreases with increasing pH. The high efficiency of nitrate removal at low pH can be attributed to the fact that nitrate has a negative charge. Since the pH_{pzc} of the adsorbent is equal to 6.4, then at pH values below pH_{pzc} the surface charge of the adsorbent is positive and cationic, and at pH values above 6.4, the adsorbent appears anionically and with a negative charge. Therefore, at pH values less than 6.4, because the adsorbent and the nitrate molecule have opposite charges, electrostatic attraction is created and adsorption takes place. Besides, at pH values higher than 6.4, the nitrate molecule has a negative charge, and adsorbent (activated carbon prepared from hard pistachio shells) due to pH_{pzc} also has a negative charge. That is, both the adsorbent and the contaminant have a negative charge, so the removal efficiency at alkaline pH is reduced.

Investigating the effect of adsorbents on adsorption processes is one of the most important issues to be considered. In this study, the adsorbent concentration was applied in the range of 0.05 to 0.30 g/L and its effect on nitrate removal efficiency was measured. It was shown as the adsorbent concentration increases due to the increase of adsorption sites, the removal efficiency increases. It can also be suggested that at a constant nitrate concentration, with an increase in the amount of adsorbent, the ratio of active sites present on the adsorbent surface to the adsorbed material molecules increases, thus increasing the removal efficiency. In contrast, at low ratios of active sites present on the adsorbent surface to the adsorbed material molecules, the adsorbent concentration decreases and as a result, the removal efficiency decreases. This is to say that with increasing the amount of adsorbent, the total capacity of active sites in the adsorbent surface is not fully used and this reduces the absorption of contaminants per unit amount of adsorbent [15, 16].

In this study, the reaction time was set in the range of 5 to 60 min and its effect on nitrate removal efficiency was measured. The results showed that the adsorption process for nitrate undergoes an increasing trend for up to 30 min and from 30 to 60 min the adsorption process reaches equilibrium and shows a relatively constant trend. To account for the effect of reaction time, it can be argued that as the reaction time increase, the probability of the contaminant molecule colliding with the adsorbent increases, and as a result, the removal efficiency increases, i.e., the contaminant residual in the solution decreases and the adsorption capacity increases [17-19].

In their study, Mohammadian-Fard et al. (2017) used orange peel as a raw material to produce activated carbon and used it to remove nitrate. They found that the optimal efficiency rate was obtained with the initial nitrate concentration of 100 mg/L, pH equal to 3, and reaction time of 150 min, and the adsorbent dosage of 2 g/L. The maximum adsorption capacity of activated carbon prepared from orange peel was 41.32 mg/g [20]. Rezaee et al. (2008) used almond shells to prepare activated carbon to remove nitrate. The results showed that under optimal conditions the initial concentration of nitrate was 15 mg/L, pH was equal to 6.2, and the reaction time was 120 min [21]. Bhatnagar et al. (2008) used coconut husk as a raw material for producing activated carbon and removing nitrate. The results of their study showed that the highest removal efficiency was obtained at the initial nitrate concentration of 30 mg/L, a pH of 5.5, a reaction time of 120 min, and a 2 g/L adsorbent. The maximum adsorption capacity of activated carbon prepared from orange peel was 41.32 mg/g. under optimized conditions, i.e. the initial nitrate concentration of 50 mg/L, adsorbent dosage of 0.2 g/L, pH equal to 5, and the reaction time of 30 minutes, the nitrate removal efficiency was 99.4% and the maximum adsorbent capacity was equal to 211.6 mg/g [22].

Isotherm studies describe the removal mechanism. In fact, isotherm studies assess the relationship between the concentration of nitrate in the reactor and the amount of nitrate adsorbed by the adsorbent (activated carbon). Among the available isotherms, the two Freundlich and Langmuir isotherm models are widely used for evaluating adsorption equilibrium. Therefore, in this study, both Freundlich and Langmuir isotherms were investigated. The correlation coefficient (R^2) for the Langmuir isotherm was higher than that of the Freundlich isotherm, indicating that the nitrate uptake process is more consistent with the Langmuir isotherm. The parameter b is a coefficient that is related to the absorption energy and as it increases, the absorption forces increase. The coefficient b is used in the Langmuir model to calculate the utility factor (R_L). When $R_L = 0$, the isotherm is irreversible and when $0 < R_L < 1$ the isotherm is desirable. Besides, when it is $R_L > 1$, the isotherm is undesirable. In the present study, the R_L coefficient was 0.056. Since the R_L value ranges from 0 to 1, it indicates the desirability of the Langmuir isotherm [23, 24].

Besides, the numerical value of q_m was equal to 211.6 mg/g, indicating the high adsorption capacity of activated carbon. The Freundlich isotherm constants are n and K_f, where n indicates the adsorption intensity and K_f indicates the adsorption capacity. A value of n between 1 and 10 indicates the optimal adsorption process. The coefficient n in Freundlich isotherm was 3.11, which was in the desired range indicating the optimal adsorption and homogeneity of the absorbent surface. Higher K_f values indicate an increase in adsorption capacity to remove contaminant molecules from the solution. In this study, K_f was calculated as 65.4 L/g.

Kinetic studies are of particular importance to investigate the reaction rate in chemical processes. The first-order kinetics shows that the adsorption process occurs in one layer of the adsorbent and the second-order kinetics shows that the multi-layer chemical adsorption of the pollutant by the adsorbent limits the adsorption process and controls the whole process [12, 24]. An assessment of these two models in the present study shows that the correlation coefficient (R^2) in the first-order kinetics model was greater than that in the first-order kinetics. This indicates that the nitrate removal process follows second-order kinetics. The value of equilibrium adsorption capacity (qe) in the second-order kinetics was equal to 161.2 mg/g. The greater the equilibrium adsorption capacity, the more desirable the process.

5. Conclusion

The present study examined the nitrate removal efficiency using activated carbon prepared from hard pistachio shells. The effect of the main operational variables including initial nitrate concentration, adsorbent dosage, pH, and reaction time on nitrate removal efficiency was studied using activated carbon prepared from hard pistachio shells. It was shown that under optimized conditions including initial nitrate concentration of 50 mg/L, adsorbent dosage of 0.2 g/L, pH equal to 5, and reaction time of 30 min, activated carbon could remove 99.4% of nitrate. The maximum adsorbent capacity was 211.6 mg/g. The nitrate adsorption process follows the Langmuir isotherm and second-order kinetics. Accordingly, it can be concluded that the adsorption process using activated carbon has a significant efficiency in removing high concentrations of nitrate and can be used as an efficient and environmentally friendly way to treat water containing this contaminant.

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