

KINETICS MODELING AND ISOTHERMS FOR ADSORPTION OF NITRATE FROM AQUEOUS SOLUTION BY WHEAT STRAW

MODELAGEM CINÉTICA E ISOTERMAS PARA ADSORÇÃO DE NITRATO DE SOLUÇÃO AQUOSA POR PALHA DE TRIGO

RESUMO

O nitrato é uma substância química incolor e inodora, com uma formulação química de NO_3 e massa média de 62,0049 g / mol. De acordo com um anúncio da organização mundial de saúde (OMS), a quantidade padrão de nitrato na água potável é de no máximo 50 ml / L (com base no nitrato). O nitrato entra no corpo e é transformado em nitrito pelas bactérias do sistema digestivo, depois entra no sistema circulatório e oxida o ferro existente na hemoglobina do sangue, que converte a capacidade de ferro de 2 para 3. Como resultado desse processo, a hemoglobina é convertida em Metahemoglobina, que tem muito menos capacidade na entrega de oxigênio. Portanto, os tecidos não podem receber oxigênio suficiente e causam uma doença chamada “metahemoglobinemia”. O objetivo deste estudo foi investigar a remoção de nitrato usando palha de trigo e determinar as isotermas e cinéticas de adsorção. Neste estudo, soluções de nitrato foram preparadas a partir de sal de nitrato de potássio. Os valores de pH das soluções foram ajustados por NaOH e HCl a uma concentração de 0,1 mol / L. O pH da solução foi ajustado para diferentes valores (4 a 13). Modelos cinéticos de Ho et al e Lagergren foram utilizados para descrever os dados. Modelos isotérmicos de Langmuir e Freundlich foram utilizados para descrever os dados. Os resultados mostraram que a capacidade máxima de palha de trigo na adsorção de nitrato ocorreu em pH = 6 e tempo de contato de 140 minutos. Modelos de equilíbrio (Langmuir e Freundlich) e não-equilíbrio (Ho et al. E Lagergren) foram utilizados para investigar o processo de adsorção. A comparação dos coeficientes de determinação entre os dados medidos e o valor obtido do modelo de Ho ($R^2 = 0,97$) e do modelo de Lagergren ($R^2 = 0,91$) mostrou que o modelo de Ho descreve melhor os dados experimentais. Além disso, a comparação da isoterma de Langmuir e Freundlich para adsorção de nitrato por palha de trigo mostrou que a isoterma de Freundlich ($R^2 = 0,98$) foi mais adequada que a isoterma de Langmuir ($R^2 = 0,83$) na descrição do processo de adsorção.

Palavras-chave: Nitrato, Ho et al., Lagergren, Langmuir, Freundlich.

ABSTRACT

Nitrate is a colorless, odorless chemical substance with a chemical formulation of NO_3^- and average mass of 62.0049 g/mol. According to an announcement of the world health organization (WHO), the standard amount of nitrate in potable water is at most 50 ml/L (based on nitrate). Nitrate enters into the body and is transformed to nitrite by digestive system's bacteria, then enters to the circulatory system and oxidizes the exiting iron in Hemoglobin of blood which converts the iron capacity from 2 to 3. As a result of this process Hemoglobin is converted to Methemoglobin which has far more less capacity in oxygen delivery. Therefore, the tissues cannot receive sufficient oxygen and it causes a disease called “Methemoglobinemia”. The objective of this study was to investigate the nitrate removal using wheat straw and determining the adsorption isotherms and kinetics. In this study, nitrate solutions were prepared from potassium nitrate salt. The pH values of the solutions were adjusted by NaOH and HCl at a concentration of 0.1 mol/L. The pH of the solution was adjusted to different values (4 to 13). Kinetics

Hedieh Ahmadpari

Graduate of Irrigation and Drainage, Department of Irrigation and Drainage, College of Aburailhan, University of Tehran, Iran.
Email:
h.ahmadpari@gmail.com

Mohsen Eskafi Noghany

Expert, Department of irrigation and drainage, College of Aburailhan, University of Tehran, Iran.
Email: m_skafi@ut.ac.ir

Behnam Rigi Ladez

M.Sc. Student of Irrigation and Drainage, University of Zabol, Iran, Email:
behnam.rigi@gmail.com

Babak Mehrparvar

Master of Civil Engineering- Hydraulic Structures, University of Mohagheg Ardebili, Iran. Email:
Babak_mehrparvar@yahoo.com

Saeed Momeni

Expert of Central Laboratory, College of Aburailhan, University of Tehran, Iran. Email:
s_momeni@ut.ac.ir

models of Ho et al and Lagergren were used to describe the data. Isotherm models of Langmuir and Freundlich were used to describe the data. The results showed that the maximum capacity of wheat straw in nitrate adsorption occurred at pH=6 and contact time 140 minutes. Equilibrium models (Langmuir and Freundlich) and non-equilibrium (Ho et al. and Lagergren) were used to investigate the adsorption process. Comparing the determination coefficients between measured data and obtained value from Ho's model ($R^2= 0.97$) and Lagergren model ($R^2= 0.91$) showed that the Ho's model describes experimental data better. Also, comparing the Langmuir and Freundlich isotherm for nitrate adsorption by wheat straw showed that Freundlich isotherm ($R^2= 0.98$) was more proper than Langmuir isotherm ($R^2= 0.83$) in describing adsorption process.

Keywords: Nitrate, Ho et al., Lagergren, Langmuir, Freundlich

1. Introduction

Nitrate is one of the most common chemical pollutants in groundwater. Increasing the pollution of surface water and groundwater by nitrate is an important motive for finding solutions with minimum environmental impacts to eliminate them. The surface adsorption method is considered as one of the most effective methods for the removal of nitrate from aqueous media due to relatively low operating costs and the lack of final treatment at all times.

In the surface adsorption process, the price of consuming adsorbent is one of the most important factors in the economic process. For this reason, most researchers are trying to make and choose a cheap adsorbent in the surface adsorption process. Therefore, the use of natural, low-cost and environmentally friendly adsorbents, is considered as an effective tool for achieving sustainable development. So far, much research has been done on the removal of nitrate from aqueous solutions with various adsorbents, which some of them are referred to here. Farasati et al. (2013) the effect of sugarcane straw and *Phragmites australis* anion exchanger nano adsorbents investigated for removal of nitrate from aqueous solutions.

The effects of operating conditions such as pH, contact time, adsorbent loading, initial anion concentration, and the presence of competitive ions on the adsorption performances were examined. The results showed that the equilibrium time was 2 hours and the pH was 6. With pH of the solution varying from 2 to 10, the nitrate removal efficiency for sugarcane straw and *Phragmites australis* nano adsorbent increased up to maximum of 45% to 76% and 60% to 86% reached at pH 6. With an increase in the nitrate concentration from 5 to 120 mg/L, the removal efficiency decreased from 86% to 66% and 90% to 67% for sugarcane straw and *Phragmites australis* nano adsorbent, respectively. For *Phragmites australis* nano adsorbent, with an increase in the adsorbent dosage from 0.1 g to 0.3 g, the removal efficiency increased from 60% to 85%, but remained almost unchanged when adsorbent dosage ranged from 0.3 g to 1 g.

For sugarcane straw nano adsorbent as the adsorbent dosage increased from 0.1 g to 0.5 g, the removal efficiency of nitrate increased from 45% to 75%, but remained almost unchanged for the increase of 0.5 g to 1 g. Adsorption kinetics of nitrate ions could most successfully be described by Freundlich isotherm.

This study indicated that sugarcane straw and *Phragmites australis* nano adsorbents could be used for the removal of nitrate ions in water treatment and *Phragmites australis* nano adsorbent has higher adsorption than sugarcane straw nano adsorbent for nitrate removal. Safdari et al (2015) investigated the efficacy of date kernel ash on removal of nitrate from aqueous solutions. In this experimental study which was conducted in vitro, the effect of initial nitrate concentration (50, 100, and 150 mg/L), initial pH (3, 5, 7, and 9), time (15, 30, 60, 120, and 180 minutes), and weight of

adsorbent (0.4, 0.6, and 0.8 g) was investigated. The nitrate concentration was measured using spectrophotometer at two wavelengths 220 nm and 275 nm. All tests and samples analysis was done per textbooks on standard methods of sewage.

The adsorbent dose increase from 0.4 g to 0.8 g in 100 mL nitrate solution with concentrations of 50 and 100 mg/L caused increase in absorption efficiency respectively from 75% to 91% and from 53% to 65%. Increase in solution's initial pH from 3 to 9 caused decrease in the absorption efficiency from 52% to 8%. The results obtained in this study obey Freundlich isotherm ($R^2=0.98$) and nitrate absorption obeys the pseudo-second order kinetics model ($R^2=0.999$). Arbabi et al (2016) investigated the almond shells magnetized by iron nano-particles for nitrate removal from aqueous solution. In This experimental study morphology of synthesized adsorbent was analyzed using FESEM and BET techniques.

The effective parameters on nitrate ion absorption process such as pH (4-8), the amount of adsorbent (0.25-1 g/L), the initial concentration of nitrate ions (25-400 mg/L) and contact time (20-100 min) were investigated. In this research, Taguchi method was applied for determining the sample size and statistical analysis. Findings of FESEM and BET techniques confirmed that magnetic nanoparticles size and specific surface area in the synthesized adsorbent were 23-27 nm and 105.480 m²/g, respectively. At optimal pH 4 and equilibrium time of 20 min, absorption efficiency increased with adsorbent increase by 1 g/L and reduction in the initial concentration of nitrate ions (85.86±4.6).

The results of adsorption equilibrium isotherms showed that nitrate absorption process follows the Langmuir isotherm ($R^2=0.924$). Divband et al. (2014) investigated the kinetics and isotherm adsorption nonlinear models for nitrate by titanium dioxide nano particles. The results showed that the maximum capacity of titanium dioxide nanoparticles in nitrate adsorption occurred at pH=5 and contact time 120 minutes.

Equilibrium models (Langmuir and Freundlich) and non-equilibrium (Ho et al. and Lagergren) were used to investigate the adsorption process. Comparing the determination coefficients between measured data and obtained value from Ho's model ($R^2= 0.98$) and Lagergren model ($R^2= 0.95$) showed that the Ho's model describes experimental data better. Also, comparing the Langmuir and Freundlich isotherm for nitrate adsorption by titanium dioxide nanoparticles showed that Freundlich isotherm ($R^2= 0.99$) was more proper than Langmuir isotherm ($R^2= 0.91$) in describing adsorption process. Naseri et al. (2013) evaluated the performance of modified pumice on removal nitrate from aqueous solution.

This fundamental and practical study was performed in batch conditions and room-temperature. Effects of the process parameters such as contact time, initial concentration and pH

were investigated. In this study, Langmuir and Freundlich isotherms was survey to adsorption reactions and to calculate the equilibrium constant. Residual nitrate concentrations determined in 220 and 275 nm using a spectrophotometer (UV/VIS) Shimadzo-1700, Japan. Results of literature indicated that removal nitrate depend on Freundlich ($R^2 > 0.998$). In the study k_f was 0.14 and amount of adsorbed nitrate was q_m (mg/g)=0.65 for mass unit of modified Pumice.

The pseudo second-order is found in the best fitness with the kinetics data. Marzi et al. (2015) investigated the characteristics of nitrate sorption onto activated carbon. In this study, nitrate sorption kinetics and isotherms, as well as the effects of contact time, initial concentration, pH and temperature on nitrate sorption onto activated carbon were investigated.

The surface characteristics of activated carbon were also studied, through FTIR and SEM techniques. Two simplified kinetics models, namely: pseudo-first and pseudo-second orders were tested to investigate the sorption mechanisms and while two isotherm models namely Freundlich and Langmuir employed to describe the equilibrium sorption of nitrate onto activated carbon. The results revealed that the amount of nitrate sorption increased with time and reached its maximum after ten minutes past. Maximum nitrate sorption occurred in a neutral pH figure, and with either increase or decrease in the pH level, the amount of sorption being decreased.

The amount of nitrate sorption increased with a decrease in temperature, level, the depicting the exothermic nature of sorption. A comparison of the coefficient of determination of the fitted equations indicated that pseudo-second order equation ($R^2=1.000$) was better fitting than pseudo-first order equation ($R^2=0.839$) for description of nitrate sorption data. Sorption isotherm was proper, as described by Langmuier model ($R^2=0.998$) and the maximum sorption parameter equaled 8.93 mg/g of activated carbon. Nemati sani et al. (2014) investigated the removal of nitrate from aqueous solutions using *Saccharomyces cerevisiae* biosorbent.

This research is a laboratory study. These researchers studied the influence of process variables such as adsorbent dose, initial NO_3 concentration, pH and contact time on adsorption process. Langmuir and Freundlich isotherms and adsorption kinetics was also studied. Most of the experiments were done with 50 mg/L of initial nitrate. Our results showed that the maximum NO_3 removal efficiency was achieved at pH = 4, adsorbent dose 1 g/100 ml and contact time 20 min. The result showed that the nitrate adsorption by the *Saccharomyces cerevisiae* followed Langmuir isotherm and second- order kinetics. Norisepehr et al. (2013) compared the chitosan function as adsorbent for nitrate removal using synthetic aqueous solution and drinking water. This experimental study is applied to the nitrate removal using chitosan in laboratory scale at ambient temperature and the design of the system was Batch.

Effects of parameters such as pH, contact time, initial concentration and adsorbent concentration of nitrate on nitrate removal from aqueous solution was studied. Function of chitosan in synthetic aqueous solution and drinking water according to the slurry system results, the optimum condition was obtained at pH=4, 20 min contact time and increasing the initial concentration of nitrate enhance the adsorption capacity of chitosan. Also optimum dosage of adsorbent was obtained at 0.5 g/L.

The data obtained from the experiments of adsorbent isotherm were analyzed using Langmuir and Freundlich isotherm models. The Langmuir equation was found to be the best fitness with the experimental data ($R^2 > 0.93$). The objective of this study was to investigate the nitrate removal using wheat straw and determining the adsorption isotherms and kinetics.

2. Materials and methods

Wheat straw was obtained from farms of Tehran province and in order to increase the accuracy of the experiment, weed straw was removed from the straw. After clearing the wheat straw, the grass was washed four times with water and twice with distilled water and dried in an oven at 80 °C for 24 hours. Storage solutions (1000 mg/L) were prepared using potassium nitrate salt. Then solutions were made at concentrations of 1, 2, 5, 10, 20, 40 and 50 mg/L of the main storage solution. In all experiments, the volume of the solution used will be 50 ml.

The pH values of the solutions were adjusted by NaOH and HCl at a concentration of 0.1 mol/L. In order to determine the optimum pH of nitrate adsorption by wheat straw, first 10 beaker of 200 ml washed with distilled water and 3 molars nitric acid solution and in each beakers is poured 1 gram of adsorbent. Then add 100 ml of solution with a concentration of 20 mg/L to each beaker. The pH of the solution was adjusted to different values (4 to 13).

The solution is placed at room temperature for 24 hours on an incubator shaker at a speed of 150 rpm. After this time, the adsorbent separation from the solution is carried out by the filter paper and the concentration of the solution is determined. Then the amount and adsorption efficiency are determined from relations 1 and 2 (Bhatnagar et al., 2010; Hekmatzadeh et al., 2013).

$$q_e = ((C_o - C_e) / (m)) \times V \quad (1)$$

$$\%R = ((C_o - C_e) / (C_o)) \times 100 \quad (2)$$

Initial concentration of nitrate in solution(mg/l) = C_o ; Concentration of nitrate in solution after mixing time(mg/l) = C_e ; Adsorbent mass(g)= m ; Volume of the solution(L)= V ; Amount of adsorption(mg/g) = q_e ; Adsorption efficiency (%)= R

For optimal adsorbent mass determination experiments, the amount of 1, 2, 3, 4, 5, 10, 15, 20, 30, 40 and 50 g of wheat straw is added to 100 mL of solution at a concentration of 20 mg/L. The pH of the solution is adjusted to the optimum amount and then placed on a shaker at 150 rpm for 120 min. After this time, the adsorbent separation from the solution is carried out by the filter paper and the concentration of the solution is determined. Then the amount and adsorption efficiency are determined from relations 1 and 2.

Obtaining adsorption isotherm is a suitable method for determining adsorbent potentials. The adsorption isotherm curves are able to quantitatively evaluate the behavior and adsorption performance of natural adsorbents for a substance at a time. Equilibrium adsorption isotherms are equations that show the distribution of matter adsorbed between the soluble and absorbed phase in the equilibrium condition and is a characteristic for the system at a specific temperature.

To describe the equilibrium state, two parameters q_e and C_e are used, where q_e is the amount of matter adsorbed per unit weight of the adsorbent and C_e is the concentration of the remaining part in the solution. To perform adsorption isotherm tests, add 1 gram of wheat straw to 100 ml of solution at various concentrations (1, 2, 5, 10, 20, 40 and 50 mg/L), and the shaker is placed at a speed of 150 rpm for 120 minutes.

After this time, the adsorbent separation from the solution is carried out by the filter paper. Then the Langmuir and Freundlich models are used to describe the data. The Langmuir model shows a monolayer adsorption on the homogeneous surface without the reaction between adsorbed molecules and uniform energies of adsorption on the surface. The Langmuir adsorption isotherm is represented by Equation 3 (Langmuir, 1916).

$$q_e = \frac{q_m b c_e}{k_1 + k_1 c_e} \quad (3)$$

Concentration of adsorbed substance in equilibrium condition in the liquid phase (mg/L) = C_e ; The amount of ion adsorbed per unit mass of the adsorbent in equilibrium condition (mg/g) = q_e ; Adsorption capacity in solid phase (mg/g) = b ; Adsorption coefficient = k_1

Freundlich isotherm is an experimental model for explaining the multilayer adsorption by heterogeneous energy distribution with the reaction between the adsorbed molecules. The Freundlich adsorption isotherm is represented by Equation 4 (Freundlich, 1906).

$$q_e = \frac{x}{m} = k_f c_e^{\frac{1}{n}} \quad (4)$$

The isotherm coefficient in relation to the amount of adsorbed according of L/g = k_f ; The adsorption intensity is that changes with the non-uniformity of the material = $1/n$

One of the important studies in the adsorption process is the study of the effect of contact time on adsorption amount, which is known as kinetics studies. In order to study the mechanisms for controlling the adsorption process, the first-order kinetics models (Lagergren) and second-order kinetics models (Ho et al) will be investigated. The Lagergren kinetics model is represented by Equation 5 (Lagergren, 1898).

$$\text{Log}(q_e - q_t) = \log q_e - (k_1 t / 2.303) \quad (5)$$

The equilibrium adsorption capacity as $\text{mg/g} = q_e$; The amount of nitrate adsorbed at time t according to $\text{mg/g} = q_t$; The adsorption constant is according to $\text{min}^{-1} = k_1$

The Ho et al. kinetics model is represented by Equation 6 (Lagergren, 1898).

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2 + \frac{t}{q_e}} \quad (6)$$

The equilibrium adsorption capacity as $\text{mg/g} = q_e$; The amount of nitrate adsorbed at time t according to $\text{mg/g} = q_t$; The adsorption constant is according to $\text{g. mg}^{-1} \text{min}^{-1} = k_2$

The efficiency of all models was evaluated using Root Mean Square Error (RMSE) and Coefficient of Determination (R^2) statistic parameters. The statistical indices RMSE and R^2 are defined as equations 7 and 8.

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (s_i - o_i)^2}{n}} \quad (7)$$

$$R^2 = \left(\frac{\sum_{i=1}^n (o_i - \bar{o})(s_i - \bar{s})}{\sqrt{\sum_{i=1}^n (o_i - \bar{o})^2 \times \sum_{i=1}^n (s_i - \bar{s})^2}} \right)^2 \quad (8)$$

The RMSE value indicates how much the predictions have estimated the measurements more or less. Whatever the value of the indicator is closer to zero, the better (the difference between the predicted and measured values is lower) (Ahmadpari et al., 2019). The well-known R^2 statistic, or the (multiple) coefficient of determination, pertains to the proportion of variance in the response variable explained by a fitted model relative to simply taking the mean of the response. In other words, it describes how well the model fits the data. An R^2 close to 1 implies an almost perfect relationship between the model and the data, whereas an R^2 close to 0 implies that just fitting the mean is equivalent to the model fitted (Saunders et al., 2012).

3. Results and discussion

Figure 1 shows the effect of PH on nitrate adsorption. As already mentioned, the range of PH is 4 to 13. Figure 1 shows that the maximum efficiency of nitrate adsorption (92%) is at $\text{pH} = 6$.

With increasing pH, more than 6, the adsorption efficiency was reduced and at least it (12%) was observed at pH=13. In low pH levels, the adsorbent surface has a positive charge, which increases the adsorbent tendency to absorb nitrate ions that have a negative charge (Olgun et al., 2013). In high pH levels, OH⁻ ions compete with nitrate ions to absorb in adsorbent positions and by occupying adsorbent sites, reduce the adsorbent capacity in nitrate adsorption (Divband et al., 2014). In addition, at high pH values, negative charge increases in the adsorbent surface and reduce the nitrate adsorption efficiency.

Figure 1-Changes in pH relative to nitrate adsorption efficiency by wheat straw

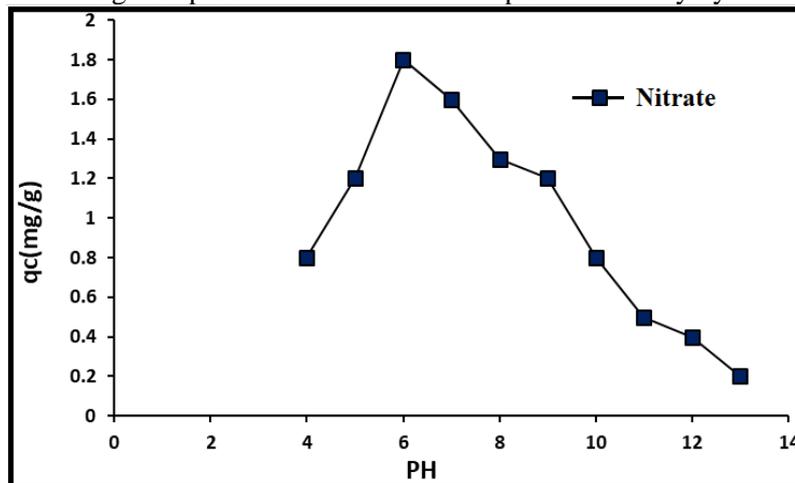


Figure 2 shows the effect of adsorbent amount on the adsorption efficiency of nitrate with a concentration of 20 mg/L. Experiments were performed in solutions of 100 ml volume. The results showed that by increasing the amount of adsorbent from 1 g to 10g, the adsorbent contact increases with nitrate ions and increases their adsorption. By increasing the amount of adsorbent (greater than 10 g), the nitrate adsorption efficiency is reduced. This is due to the fact that, by increasing the amount of adsorbent in the solution, the specific surface of the adsorbent particles decreases and the nitrate adsorption efficiency decreases by this adsorbent.

Figure 2-Changes in adsorbent amount relative to nitrate adsorption efficiency by wheat straw

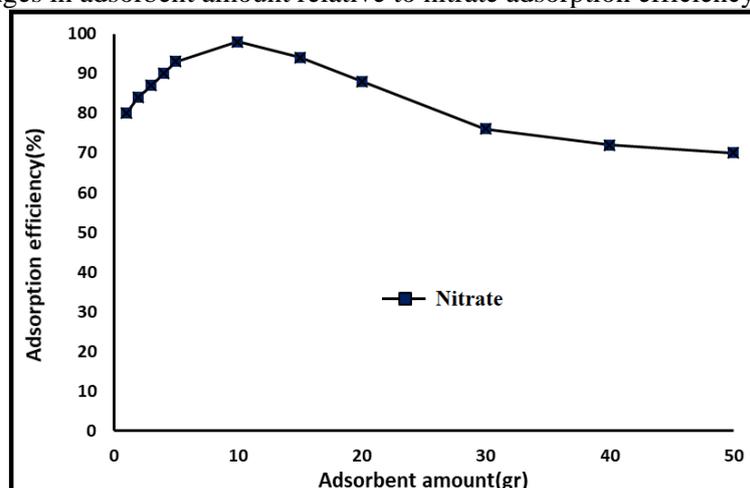


Figure 3 shows the fitting of kinetics models of nitrate adsorption by wheat straw in optimum pH. Also, the fitting results of the models are presented in Table 1. The comparison of the results shows that Ho et al. model with better determination coefficient ($R^2=0.97$) and less root mean square error (RMSE=0.08) compared to the Lagergren model ($R^2=0.91$, RMSE=0.11) describes experimental data better. Also, the results showed that the Lagergren model was more successful in estimating the value of q_e (1.85 mg/g) compared to Ho et al. model (1.94 mg/g). According to Fig. 3, the amount of adsorption increases with increasing contact time. Also, by increasing the contact of nitrate ions with adsorbent, the amount of adsorption increases. At 140 min after contact of wheat straw and nitrate solution, the adsorption process reaches equilibrium. Increasing the contact time after this time does not affect the amount of adsorption.

Table 1-Parameters of kinetics models of nitrate adsorption by wheat straw

$q_{\text{experimental}}$	Lagergren model				Ho et al. model			
	RMSE	R^2	K_1	q_e	RMSE	R^2	K_2	q_e
1.87	0.11	0.91	0.05	1.85	0.08	0.97	0.04	1.94

Figure 3 - The fitting of kinetics models on experimental data of nitrate adsorption by wheat straw

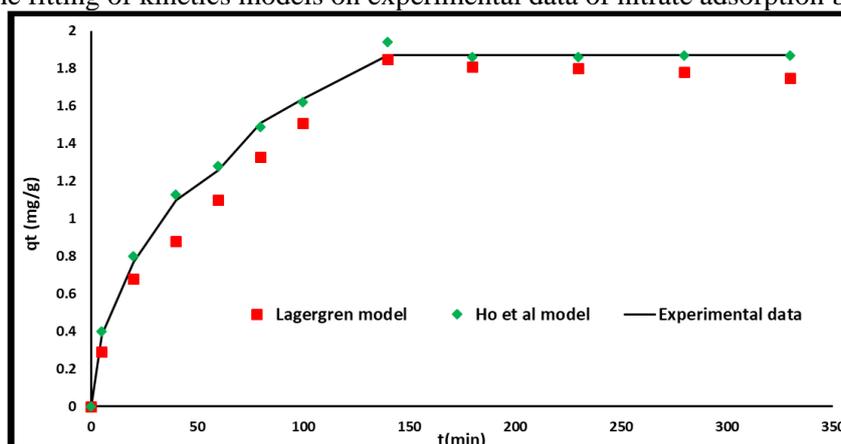
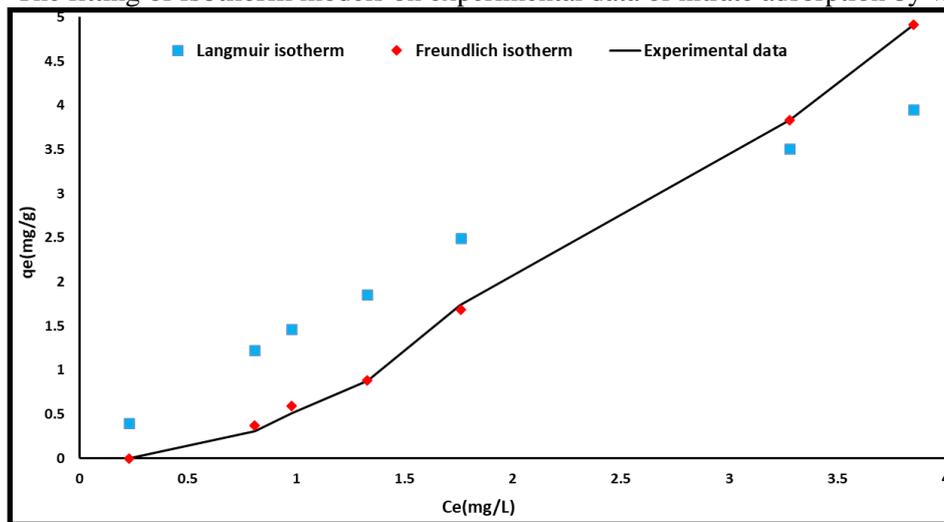


Figure 4 shows the fitting of isotherm models of nitrate adsorption by wheat straw. Also, the fitting results of the models are presented in Table 2. Comparing the Langmuir and Freundlich isotherm for nitrate adsorption by wheat straw showed that Freundlich isotherm ($R^2=0.98$, RMSE=0.15) was more proper than Langmuir isotherm ($R^2= 0.83$, RMSE=0.43) in describing adsorption process. The parameter b in the Langmuir model expresses the maximum adsorbent capacity for nitrate adsorption at its surface. In this study, this parameter was 13.36 mg/g.

Table 2-Parameters of isotherm models of nitrate adsorption by wheat straw

Freundlich isotherm				Langmuir isotherm			
RMSE	R^2	K_f	n	RMSE	R^2	K_L	b
0.15	0.98	0.65	0.64	0.43	0.83	0.17	13.36

Figure 4 - The fitting of isotherm models on experimental data of nitrate adsorption by wheat straw



4. Conclusion

According to the results of this study, optimum pH for nitrate adsorption by wheat straw is 6. The results of adsorption kinetics experiments showed that as the contact time increases, the absorption efficiency increases, and the balance time for this study is 140 minutes. At the optimal balance time and pH, the maximum adsorption value was calculated 1.87 mg/g. Also, the results showed that Ho et al. model describes adsorption kinetics data better than Lagergren model. The results of isotherm studies showed that the Freundlich model has a better fit for adsorption test data.

References

- Ahmadpari, H., Shokoohi, E., Falahpour Sichani, B., Namdari Gharghani, E., Rigi Ladez, B. (2019). Evaluation of the most appropriate statistical distribution for monthly rainfall prediction in the Zarrineh river watershed, *Specialty Journal of Biological Sciences*, 5 (2), 1-9.
- Arbabi, M., Hemati, S., Raygan, S., Sedehi, M., Khodabakhshi, A., Fadaei, A. (2016). Evaluation of almond shells magnetized by iron nano-particles for nitrate removal from aqueous solution: study of adsorption isotherm. *Journal of Shahrekord university of medical sciences*, 17 (6), 92-102.
- Bhatnagar, A., Kumar, E., & Sillanpää, M. (2010). Nitrate removal from water by nano-alumina: Characterization and sorption studies. *Chemical Engineering Journal*, 163(3), 317-323.
- Divband, S., Shirazi, p., Divband, L, Azadi, S., Tishehzan, P. (2014). Kinetics and isotherm adsorption nonlinear models survey for nitrate by titanium dioxide nano particles, *Journal of water and sustainable development*, 1(1), 35-41.
- Farasati, M., Jafarzadeh, N., Boroomand, S., Moazed, H., Abedi Kupaei, J., Seyedian, M. (2013). Use of agricultural nano adsorbents for nitrate removal from aqueous solutions, *Iran-water resources research*, 8(3), 28-38.
- Freundlich, H. M. F. (1906). Over the adsorption in solution. *J. Phys. Chem*, 57(385471), 1100-1107.
- Hekmatzadeh, A. A., Karimi-Jashni, A., Talebbeydokhti, N., & Kløve, B. (2013). Adsorption kinetics of nitrate ions on ion exchange resin. *Desalination*, 326, 125-134.
- Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances. *J. of Kungliga Svenska Vetenskapsakademiens Handlingar*, 24(4), 1-39.
- Langmuir, I. (1916). The constitution and fundamental properties of solids and liquids. II Liquids. *Journal of the American Chemical Society*, 38(11), 2221-2295.

- Marzi, M., Farahbakhsh, M., Shahbazi, K. (2015). Characteristics of nitrate sorption onto activated carbon. *Iranian journal of soil and water research*, 46(3), 545-553.
- Naseri, S., Heibati, B., Asadi, A., Gholestani Far, H., Dargahi, A. (2013). Performance evaluation of modified pumice on removal nitrate from aqueous solution: kinetics studies and adsorption isotherm, *Toloo-e-behdasht*, 12(1), 143-154.
- Nemati sani, O., Sadeghi, A., Dehghan, A A., Asadzadeh, S., Dolatabadi, M. (2014). Removal of nitrate from aqueous solutions using *Saccharomyces cerevisiae* biosorbent: adsorption isotherms and kinetics. *Journal of north Khorasan university of medical sciences*, 6 (2), 441-449.
- Norisepehr, M., Golbaz, S., Jarghi, S. (2013). Comparison of chitosan function as adsorbent for nitrate removal using synthetic aqueous solution and drinking water, *Journal of environmental health engineering*, 1 (1), 11-19.
- Olgun, A., Atar, N., & Wang, S. (2013). Batch and column studies of phosphate and nitrate adsorption on waste solids containing boron impurity. *Chemical engineering journal*, 222, 108-119.
- Safdari, M, Qhaneian, M T., Ehrampoush, M H., Babae, A R., Emamjomeh, M M., Zareii, S. (2015). Study of efficacy of date kernel ash on removal of nitrate from aqueous solutions (isothermic and kinetics study), *Journal of Shahrekord university of medical sciences*, 16 (6), 48-56.
- Saunders, L. J., Russell, R. A., & Crabb, D. P. (2012). The coefficient of determination: what determines a useful R² statistic? *Investigative ophthalmology & visual science*, 53(11), 6830-6832.