KINETICS AND THERMODYNAMIC STUDY OF NITRATE ADSORPTION ON GRANULAR FERRIC HYDROXIDE

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ABSTRACT

This study explored the feasibility of using granular ferric hydroxide as adsorbent for the removal of NO$_3^-$-N. Optimum conditions for NO$_3^-$-N removal were found to be pH 5.0 and equilibrium time 80min. The equilibrium sorption isotherm was better described by Langmuir sorption isotherm model. The maximum sorption capacity of granular ferric hydroxide was 4.254mg/g at 298K. A comparison of four kinetic models applied to the adsorption of NO$_3^-$-N was evaluated. The experimental data fitted well the pseudo-second-order kinetic model. ∆H$_0$ and ∆G$_0$ all suggested that the adsorption of NO$_3^-$-N onto granular ferric hydroxide was physisorption.

KEYWORDS: nitrate removal; granular ferric hydroxide; Adsorption isotherm; kinetics; thermodynamics

1. INTRODUCTION

In many parts of the world, groundwater serves as the sole source of drinking water in rural communities and urban areas. Nitrate, due to its high water solubility, is possibly the most widespread groundwater contaminant in the world, imposing a serious threat to drinking water supplies and promoting eutrophication. Excess nitrate in drinking water may cause two adverse health effects: a blue baby disease (methemoglobinemia), especially in infants, and the potential formation of carcinogenic nitrosamines [1].

Traditional methods for nitrogen removal from wastewater are biological processes (denitrification, nitrification), chemical processes (breakpoint chlorination, selective ion exchange) and physical operation (ammonia stripping). Other operations or processes are conventional treatment (primary, secondary), biological processes (bacterial assimilation, harvesting of algae, oxidation ponds), chemical processes (chemical coagulation, adsorption), physical operations (ammonia stripping, electrodialysis, filtration, reverse osmosis), land application (irrigation rapid infiltration, overland flow) [2].

The application of most of these methods on commercial scale is limited due to high operational and maintenance costs, secondary pollution and complicated procedure involved in the treatment. Comparatively, adsorption process seems to be a more attractive method for the removal of aquatic pollutants due to its simple design and ease of operation [1]. In recent years, considerable attention has been paid on economic and environmental concerns to the study of using different types of low-cost sorbents such as carbon based adsorbents [3]; clay adsorbents [4]; layered double hydroxides [5]; agricultural waste such as sugarcane bagasse and rice hull [6], wheat straw [7]; industrial waste such as original and activated red mud [8].

The objective of this work was to study the feasibility of using granular ferric hydroxide (GFH) [9] as an adsorbent for NO$_3^-$-N removal from wastewater. It has been successfully applied for removal of bromate [10], fluoride [9], arsenic [11], phosphorus [12] and natural organic matters [13] from water.

In the present work, the effects of various operating parameters, such as NO$_3^-$-N concentration, solution pH, and temperature, were studied and optimized by batch sorption experiments. Sorption isotherms, kinetics and thermodynamic parameters were also evaluated for the sorption of NO$_3^-$-N onto GFH. In addition, the kinetics and thermodynamics studies were used to gain insight on potential sorption mechanism of NO$_3^-$-N by GFH.

2. MATERIALS AND METHODS

2.1. Materials

GFH is predominately akaganeite, a poorly crystallized iron oxide. The specific surface area is reported to be 280 m$^2$/g, the point of zero charge (pH$_{pzc}$) is between 7.5 and 8.0, the water content is 50% by weight. According to the manufacturer’s references (GEH Wasserechemie, Osnabrück), the applied material had a grain size range of 0.32-2.0mm [12]. It was sieved to obtain a fraction with grain size ranges between 0.1 and 1.0mm for batch study. This fraction was then washed several times with deionised water and dried at room temperature for 16h. Finally samples were transferred to glass bottles for further study. Stock solution of NO$_3^-$-N (300mg/L) was
prepared by dissolving KNO₃ in deionised water and diluted to 10-120mg/L for further use. All reagents used were analytical reagent grade.

2.2. Batch Study

The adsorption of NO₃⁻-N onto GFH was studied at room temperature (298±2K) by batch experiments, except for investigation of temperature effect. 200mL of nitrate solution of fixed NO₃⁻-N concentration was taken into 250 mL of conical flask, whereafter, the conical flask was agitated with 1g of adsorbent for a specified period of contact time in a temperature controlled shaker (150 rpm). When equilibrium attained, samples were then filtered through 0.45µm filter paper and analyzed for residual NO₃⁻-N concentration. The removal percentage at equilibrium (10-50mg/L) at a constant adsorbent dose of 5 g/L. The adsorption of NO₃⁻-N was studied by varying the initial NO₃⁻-N concentrations (10-50mg/L) at a constant adsorbent dose of 5 g/L. The effect of pH on the adsorption of NO₃⁻-N onto GFH was studied by varying the initial solution pH from 1 to 11 using 0.1 M NaOH and HCl solutions. To investigate the effect of temperature, experiments were conducted at 283K, 288K, 293K, 298K, 303K and 308K, respectively. Isotherm experiments were conducted by varying the initial NO₃⁻-N concentration from 10 to 120 mg/L at 298K, while maintaining the initial pH at 5.0. The kinetic analysis of the adsorption data was based on reaction kinetics of pseudo-first-order, pseudo-second-order, Weber and Morris intra-particle diffusion model and Bangham’s pore diffusion model.

The amounts of NO₃⁻-N adsorbed were calculated at various time t (qt in mg/g) and at equilibrium (qe in mg/g) as follows:

\[ q_t = \frac{(C_0 - C_t)V}{m} \]  
\[ q_e = \frac{(C_0 - C_e)V}{m} \]

where \( C_0 \) and \( C_t \) are the initial and equilibrium concentrations of NO₃⁻-N in solution(mg/L), \( C_e \) is the concentration of NO₃⁻-N in solution at time 't' (mg/L), \( V \) is the volume of the solution(L), and \( m \) is the mass of the adsorbent(g). Also, the removal percentage at equilibrium (R%) was calculated by equation (3):

\[ R\% = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \]

3. RESULTS AND DISCUSSION

3.1. Effect of Contact Time and Initial NO₃⁻-N Concentration

Due to the fact that all adsorbent sites were vacant, the adsorption process, which can be seen from Figure 1, was rapid at the beginning, whereafter, the NO₃⁻-N adsorbed by GFH decreased significantly. This behavior may be attributed to fewer adsorption sites and lower NO₃⁻-N concentration. It can also be seen that equilibrium was established at about 80min. The NO₃⁻-N uptake by GFH increased from 0.8385mg/g to 2.639mg/g when the initial NO₃⁻-N concentration increased from 10 to 50mg/L. This phenomenon resulted from the fact that along with an increase in the initial NO₃⁻-N concentration, the driving force of the concentration gradient increased. Such phenomenon is common in a batch reactor with either constant adsorbent dose and varying initial adsorbate concentration or vice versa [15].

It was also observed from the sorption data that the sorption percentage decreased with an increase of initial NO₃⁻-N concentration. The removal percentage decreased from 47.8% to 27.9% as the initial concentration increased from 10 mg/L to 50 mg/L. For a given adsorbent dose, the total number of available adsorption sites is fixed thereby adsorbing almost the same amount of adsorbate, thus resulting in a decrease in the removal percentage of the adsorbate along with an increase in initial adsorbate concentration.

![Figure 1](image-url) - Effect of contact time and initial concentration on NO₃⁻-N removal (initial pH: 5, adsorbent dose: 5g/L, shaking speed: 150 rpm, temperature: 298K).

3.2. Effect of pH

As shown in Figure 2, pH value of NO₃⁻-N solution significantly influenced the adsorption of NO₃⁻-N onto GFH. The effect of pH on adsorbate removal was dependent on the pH point of zero charge (pHpzc) of adsorbent [16]. The GFH surface was positive charge when pH was above the pHpzc of GFH. The point of zero charge (pHpzc) is between 7.5 and 8.0 [12].

Figure 2 showed that the amount of NO₃⁻-N adsorbed by GFH increased as the pH increasing from 1.0 to 5.0. This phenomenon can be explained by the electrostatic attraction between NO₃⁻ ions and positively charged surface of GFH. The NO₃⁻-N removal was very low when the pH went below 3, this may be resulted from dissolving of GFH under extremely acidic conditions. The amount of NO₃⁻-N adsorbed by GFH fell sharply as the pH went
above 7.0, this result was due to the electrostatic repulsion of NO$_3^-$ ions by the negatively charged surface of GFH at high pH and the competition for the active sites with OH$^-$ ions. The maximum adsorption of NO$_3^-$-N was found to be 1.998 mg/g at pH 5, only 0.2959 mg/g and 0.1233 mg/g was adsorbed at pH 1 and 11 respectively, therefore the acidic and alkaline pH conditions were all going against the NO$_3^-$-N removal. When the pH equaled to pH$_{zpc}$, the surface of GFH almost had no charge. Moreover, strong hydrogen bonds hindering the adsorption were formed among high density of hydroxyl groups on surface of GFH, so that it could not reach the maximum adsorption capacity under neutral conditions.

3.4. Adsorption Isotherm Studies

When the initial NO$_3^-$-N concentration was 30 mg/L, the adsorption capacity of GFH is estimated to be 2.207 mg/g to 1.887 mg/g at the temperature decreasing from 308 K to 283K. K. Banerjee et al. [17] studied that at an equilibrium As(V) concentration of 10 mg/L, the adsorption capacity of GFH to As(V) is estimated to be 1.1mg/g at 293K, when the particle size of the GFH media ranged between 0.32 and 2mm. M. Ernst et al. [12] investigated that at equilibrium concentrations of PO$_4^{3-}$-P ranging between 1 and 1.5 mg/L and pH 7-7.2, accumulated loadings were 20-25 mg/g.

Most widely tested isotherms for adsorption process are Langmuir and Freundlich models [18, 19], which were given by equation (4) and equation (6). The experimental data corresponding to Figure 4 were processed for Langmuir and Freundlich models.

\[
\text{Langmuir} : \frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{bC_e} \tag{4}
\]

Where, $q_{\text{max}}$ is the Langmuir constant representing maximum monolayer adsorption capacity (mg/g) and $b$ is the Langmuir constant related to the energy of adsorption (L/mg). The plot between $1/q_e$ versus $1/C_e$ for the adsorption of NO$_3^-$-N was shown in Figure 5(a). The plot was found linear with a good correlation coefficient (>0.99) indicating the applicability of Langmuir model in the present study, which suggested that NO$_3^-$-N was adsorbed in the form of monolayer coverage on the surface of the GFH [20]. The values of monolayer capacity $q_{\text{max}}$ and Langmuir constant ($b$) were calculated from the intercept and slope of the plot and were given in Table 1.

According to Hall et al. [21], the essential features of the Langmuir isotherm can be expressed in terms of $R_L$, a dimensionless constant referred to separation factor or equilibrium parameter, $R_L$ is calculated by equation (5).

\[
R_L = \frac{1}{1 + bC_0} \tag{5}
\]
FIGURE 5 - Isotherms modeling of NO₃--N adsorption on GFH (initial pH: 5, contact time: 200min, adsorbent dose: 5g/L, shaking speed: 150rpm): (a) Langmuir isotherm (b) Freundlich isotherm.

TABLE 1 - Langmuir and Freundlich constants of NO₃--N adsorption on GFH at 298K (initial NO₃--N concentration: 30mg/L, adsorbent dose: 5g/L, initial pH: 5.0, shaking speed: 150 rpm)

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</tr>
<tr>
<td>b (L/mg)</td>
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</tr>
<tr>
<td>Rₑ</td>
<td>0.4314</td>
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<tr>
<td>R²</td>
<td>0.9930</td>
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<tr>
<td>Freundlich</td>
<td></td>
</tr>
<tr>
<td>K((mg/g) (L/mg)^n)</td>
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<tr>
<td>1/n</td>
<td>0.4821</td>
</tr>
<tr>
<td>R²</td>
<td>0.9768</td>
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</table>

\[ Rₑ = \frac{1}{1 + bC₀} \quad \text{(5)} \]

where, \( b \) is the Langmuir constant. The value of \( Rₑ \) indicates the nature of the isotherm to be irreversible (\( Rₑ=0 \)), favorable (\( 0<Rₑ<1 \)) and unfavorable (\( Rₑ=1 \)).

It can be seen from Table 1 that the value of \( Rₑ \) lies between 0 and 1, which suggests the Langmuir adsorption isotherm is favorable.

Freundlich: \[ \text{lg}qₑ = \text{lg} K + \frac{1}{n} \text{lg} Cₑ \quad \text{(6)} \]

Where, \( K \) and \( n \) are the Freundlich constants characteristic of the system. \( K \) and \( n \) are indicators of adsorption capacity and adsorption intensity, respectively [22]. For \( 1/n \) value in the range of 0.1-1, adsorption is favorable [23]. The plot of log \( qₑ \) versus log \( Cₑ \) for the adsorption of NO₃--N was shown in Figure 5(b). The values of \( 1/n \) and \( K \) were obtained from the slope and intercept of the linear Freundlich plot and both were listed in Table 1. The \( R² \) value was found less than 0.99 indicating that Freundlich model was not applicable to the present study.

TABLE 2 - Kinetic parameters for the removal of NO₃--N by GFH and calculated \( qₑ(cal) \) and experimental \( qₑ(exp) \) values for different initial NO₃--N concentrations.(initial pH: 5.0, adsorbent dose: 5g/L, contact time: 200min, shaking speed: 150rpm, temperature: 298 K)

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<td>( qₑ(exp) ) (mg/g)</td>
<td>( k₁ ) (1/min)</td>
<td>( qₑ(cal) ) (mg/g)</td>
<td>( R² )</td>
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<tr>
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<td>( k₂ ) [mg/(g·min)]</td>
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<td>( k_{det} ) [mg/(g·√min)]</td>
<td>( R² )</td>
<td>( k_{det} ) [mg/(g·√min)]</td>
<td>( R² )</td>
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<td>0.947</td>
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<tr>
<td>( C₀ ) (mg/L)</td>
<td>( k₀ ) [mL/(g·L)]</td>
<td>( \alpha )</td>
<td>( R² )</td>
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<tr>
<td>10.00</td>
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<td>0.210</td>
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<td>1.238</td>
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<td>0.923</td>
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3.5. Sorption Kinetics

In order to investigate the adsorption mechanism of NO$_3^-$-N onto GFH, four kinetic models including pseudo-first-order, pseudo-second-order, Weber and Morris intraparticle diffusion model and Bangham’s pore diffusion model had been applied at three different initial NO$_3^-$-N concentrations (10, 30, 50mg/L). The applicable models had been discussed in detail below and modeling parameters were provided in Table 2. Figure 6 shows the plots of the linearized form.

3.5.1. Pseudo-first-order model

The Lagergren’s rate equation is one of the most widely used rate equation to describe the adsorption of an adsorbate from liquid phase [24]. The pseudo-first-order Lagergren equation is given as

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]  

(7)

where, $q_e$ and $q_t$ are the amount of NO$_3^-$-N adsorbed (mg/g) at equilibrium and at time $t$ (min), respectively, and $k_1$ (1/min) is the rate constant of pseudo-first-order kinetic. A straight line of log ($q_e$-$q_t$) versus $t$ (Figure 6(a)) suggested the applicability of this kinetic model. The slope and intercept of the plot were used to calculate $k_1$ and $q_e$(calculated) and both were shown in Table 2 along with correlation coefficient ($R^2$) values and $q_e$(experimental). From the data, $q_e$(calculated) and $q_e$(experimental) values were not in agreement with each other. Therefore, the adsorption of NO$_3^-$-N on GFH was not a first-order reaction [25].

3.5.2. Pseudo-second-order model

The pseudo-second-order [26] is expressed as equation (8):

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t
\]

(8)

where, $k_2$ is the rate constant of pseudo-second-order kinetic (g/(mg·min)). The plots of $t/q_t$ versus $t$ were shown in Figure 6(b).The values of $q_e$(calculated) and $k_2$ were determined from the slope and intercept of the plot, respectively, and were compiled in Table 2 along with correlation coefficient ($R^2$) values and $q_e$(experimental). Figure 6(b) showed that $R^2$ values (>0.99) were higher than those obtained from the pseudo-first-order kinetics. In addition, theoretical and experimental $q_e$ values were in agreement. Therefore, it was possible to prove that the adsorption process followed the second-order kinetic model.

The adsorption of solute from the solution by the adsorbent is driven by four mass transport mechanisms: diffusion at bulk space, film diffusion, intra-particle diffusion and sorption into interior sites. Generally, the first and fourth steps are rapid and thus, not considered as rate-limiting steps. Therefore, film and intra-particle diffusion are major steps controlling the rate of adsorption. The Weber and Morris intra-particle diffusion model and Bangham’s pore diffusion model have been further applied to observe the diffusion mechanism [9].

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**FIGURE 6** - Kinetic models of NO$_3^-$-N adsorption on GFH (a) pseudo-first-order kinetic plots (b) pseudo-second-order kinetic plots (c) Weber and Morris intra-particle diffusion plots (d) Bangham’s pore diffusion plots.
3.5.3. Weber and Morris intra-particle diffusion model

Kinetic data were applied in intra-particle diffusion model proposed by Weber and Morris [27]:

\[ q_t = k_{id} t^{1/2} + C \]  \hspace{1cm} (9)

where, \( C \) is the intercept, related to the thickness of the boundary layer and \( k_{id} \) is the intra-particle diffusion rate constant (mg/(g·√min⁻¹)). According to this model, if the Weber and Morris plot of \( q_t \) vs. \( t^{1/2} \) gives a straight line, then the sorption process is controlled by intra-particle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. The Weber and Morris plots of NO₃⁻-N sorption on GFH were shown in Figure 6(c). There were two separate zones: first linear portion (phase I) and second linear part (phase II). In phase I approximately 30-60% of NO₃⁻-N amount totally adsorbed at equilibrium was rapidly up-taken by GFH within 10 min. This is attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surface. Phase II may be attributed to very slow diffusion of the adsorbate from the surface sites into the inner pores. Thus initial portion of NO₃⁻-N adsorption by GFH may be governed by the initial intra-particle transport of NO₃⁻-N controlled by surface diffusion process and the later part controlled by pore diffusion.

The values of \( k_{id,1} \) and \( k_{id,2} \) (intra-particle diffusion rate constants for phase I and II, respectively) obtained from the slope of linear plots were listed in Table 2 along with correlation coefficients (R²). It was evident from \( k_{id} \) values that \( k_{id,1} \) (value of phase I) is higher than \( k_{id,2} \) (value of phase II), which indicated that initial step (phase I) was rapid followed by a slow step (phase II). The intercepts of the line at each concentration failed to pass through the origin and the \( R^2 \) values at each concentration were also less than 0.999, which suggested that two or more steps were involved in the sorption process. The deviation of straight line in Weber and Morris model may be due to differences in the rate of mass transfer in the initial and final stages of adsorption [9].

3.5.4. Bangham’s model

Bangham’s equation (equation (10)) has been used to describe pore diffusion during adsorption process [28].

\[ \ln \ln \left( \frac{C_0}{C_0 - q_m} \right) = \ln \left( \frac{k_{id} m}{2.303 V} \right) + \alpha \ln t \] \hspace{1cm} (10)

where, \( C_0 \) is the initial concentration of the adsorbate in solution (mg/L), \( V \) is the volume of the solution (mL), \( m \) is the weight of adsorbent used per liter of solution (g/L), \( q_m \) (mg/g) is the amount of adsorbate retained at time \( t \). \( \alpha \) (less than 1) and \( k_{id} \) (mL/(g·L)) are constants and were calculated from the slope and intercept of the plots (Figure 6(d)) of \( \ln \ln \left( \frac{C_0}{C_0 - q_m} \right) \) against \( \ln t \). If the experimental data can be represented by this equation, then the adsorption kinetics are limited by the pore diffusion [29].

The kinetic constants obtained from the Bangham’s equation were listed in Table 2. It can be seen that the values of \( \alpha \) and \( k_{id} \) varied as a function of the initial NO₃⁻-N concentration (Cₒ). Thus, on increasing initial NO₃⁻-N concentration from 10 to 50 mg/L, the values of \( k_{id} \) decreased from 9.785 to 1.238 mL/(g/L) and the values of \( \alpha \) increased from 0.2103 to 0.5285. The experimental data did not give a good correlation for low initial NO₃⁻-N concentration (Cₒ = 10 mg/L, \( R^2 = 0.8782 \)).

3.6. Thermodynamic Study

To evaluate the thermodynamic feasibility and to confirm the nature of the adsorption process, three basic thermodynamic parameters, standard free energy change (\( \Delta G^0 \)), standard enthalpy change (\( \Delta H^0 \)) and standard entropy change (\( \Delta S^0 \)) were calculated in this study to predict the process of adsorption. The Langmuir isotherm was used to calculate thermodynamic parameters using the following equations:

\[ \Delta G^0 = -RT \ln b \] \hspace{1cm} (11)
\[ \ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \] \hspace{1cm} (12)

where, \( R \) is an universal gas constant (8.314 J/(mol·K)), \( T \) is the absolute temperature (K), and \( b \) is the Langmuir equilibrium constant (L/mol), and the values of \( b \) at different temperatures were compiled in Table 3. \( \Delta H^0 \) and \( \Delta S^0 \) were determined from the slope and intercept of the van’t Hoff plots of \( \ln(b) \) versus 1/T. [30] Figure 7 showed the van’t Hoff plot for the adsorption of NO₃⁻-N onto GFH. Table 3 presented the thermodynamic parameters at various temperatures.

![Figure 7](image-url) - Regressions of van’t Hoff plot for thermodynamic parameters.

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<tr>
<th>T(K)</th>
<th>b(L/mol)</th>
<th>( \Delta G^0 )(kJ/mol)</th>
<th>( \Delta H^0 )(kJ/mol)</th>
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</table>

TABLE 3 - The values of Langmuir constant b and thermodynamic parameters for the sorption of NO₃⁻-N by GFH using NO₃⁻-N concentration of 30mg/L.
The value of $\Delta H^\circ$ was -5.013 kJ/mol, Kara et al. [31] suggested that the $\Delta H^\circ$ of physisorption was smaller than 40 kJ/mol. Based on $\Delta H^\circ$, this study suggested that the adsorption of NO$_3$-N onto GFH was a physisorption process. Negative $\Delta H^\circ$ value suggested that the adsorption of NO$_3$-N onto GFH was exothermic, which fact was supported by the decrease in the adsorption of NO$_3$-N with the increasing of temperature. Moreover, the negative $\Delta S^\circ$ indicated that a decrease in randomness [32] at the solid-liquid interface during the adsorption of NO$_3$-N onto GFH. The $\Delta G^\circ$ values were negative at all of the tested temperatures (288-303K), confirming that the adsorption of NO$_3$-N onto GFH was spontaneous and thermodynamically favorable. Restated, a more negative $\Delta G^\circ$ implied a greater driving force of adsorption, resulting in a higher adsorption capacity. When the temperature decreased from 303 to 288K, $\Delta G^\circ$ became a high negative value, suggesting that adsorption was more spontaneous at low temperature. Generally, $\Delta G^\circ$ for physisorption is less than that for chemisorption. The former is between -20 and 0 kJ/mol and the latter is between -80 and -400 kJ/mol [30]. Therefore, the $\Delta G^\circ$ results implied that physisorption might dominate the adsorption of NO$_3$-N onto GFH.

4. CONCLUSIONS

The present study showed that it was possible to utilize granular ferric hydroxide as an adsorbent to remove NO$_3$-N from aqueous solution. The adsorption capacity of GFH for NO$_3$-N was 4.254mg/g at 298K. The removal process was highly relevant with pH and the best results were obtained at pH 5. The equilibrium data fitted better to a Langmuir model, indicating monolayer nature of NO$_3$-N sorption onto GFH. The kinetic data followed pseudo-second-order kinetics, and intra-particle diffusion played a major role in the adsorption process. The sorption of NO$_3$-N onto GFH was found to be a two steps process: the first step may be attributed to the transport of NO$_3$-N by surface diffusion and the second step was controlled by pore diffusion. The process was thermodynamically favourable, spontaneous, exothermic and physisorption in nature. Experimental data can be further used to guide and optimize pilot scale experiments that can enable the commercial exploitation of GFH for NO$_3$-N removal from drinking water and regeneration of wastewater with low NO$_3$-N concentration.

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