Nitrate Removal from Waste-Water Using Silica Nanoparticles

Phuong Kim To,1 Hoa Thai Ma,2 Lam Nguyen Hoang,3 and Tan Tai Nguyen4

1School of Medicine and Pharmacy, Tra Vinh University, Tra Vinh City 87000, Vietnam
2Department of Activated Polymer and Nano Materials Applications, School of Applied Chemistry, Tra Vinh University, Tra Vinh City 87000, Vietnam
3Biotechnology and Environment Center, School of Agriculture and Aquaculture, Tra Vinh University, Tra Vinh City 87000, Vietnam
4Department of Materials Science, School of Applied Chemistry, Tra Vinh University, Tra Vinh City 87000, Vietnam

Correspondence should be addressed to Tan Tai Nguyen; nttai60@tvu.edu.vn

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This work presented the removal of nitrate ions in aqueous solution based on silica nanoparticles (SiNPs), which were extracted from rice husk ash. The optimal conditions for nitrate ion adsorption were studied including pH, contact time, adsorbate concentration, and amount of absorbance. The surface morphological analysis showed that the SiNPs extracted (purity of 98%) were around 50 nm with a surface area of 30 m²·g⁻¹ and adsorption average pore width of 2.72 nm, offers possibility for high capability of nitrate ion removal. The experimental results showed that the nitrate ion capability of adsorption was obtained around 14.22 mg·g⁻¹ with a concentration range from 0 to 25 mg·L⁻¹ based on optimizing conditions including pH 6, contact time of 50 minutes, and SiNP dosage of 0.15 g·vol⁻¹. In addition, nitrate ion removal based on SiNPs will provide considerate benefits such as the reducing costly sample pretreatment steps, less time-consuming, and reliable methods for processing nitrate-polluted water.

1. Introduction

Nowadays, pollution of surface water by nitrate is serious problem. Using large amount of artificial fertilizers has caused the penetration of nitrates into the surface water. An increase in amount of nitrate may be associated with the increment of aquatic organism that caused water eutrophication [1]. Recently, several methods for removal of nitrogen ions in waste-water have been reported including wetland treatment system [2–4], electrodialysis [5–10], electrochemical reaction [11–16], bioreactor system [17], integration between electrodialysis and electrolysis [18, 19], catalytic oxidation-removal process [20], and anion exchange resin [21]. However, those methods seem not to be suitable for the elimination of nitrate ions due to their significant disadvantages such as complication in operation, subsequent disposal problem of the generated nitrate waste brine, and expensive and time-consuming method.

A few decades ago, adsorption processing has been investigated and widely applied for removal of nitrate ions in waste-water due to its benefits, i.e., high adsorption capacity, ease-of-use, and environmentally friendly method. For examples, several adsorption materials have been used for nitrate ion removal such as coal-fired blue gas [20], soil profiles and sediments [22], and sawdust [23–25]. However, these materials needed the pretreatment for the removal process. Therefore, it is worth to consider that silica nanoparticles (SiNPs) are promising material for removal of heavy metals [26–28] with high adsorption capability. In addition, the rice husk ash (RHA), which contains high amount of silica (approximately 90%), is the by-product of a brick-kiln industry. So, the reuse and recycling process of RHA for extraction of SiNPs is a cost-effective and environmental friendly method.

This work was designed to investigate the adsorption process of nitrate ions utilizing SiNPs, which was extracted...
from RHA. The physicochemical properties of the adsorbent were investigated, and the adsorption conditions were optimizing based on controllable parameters including pH, adsorbent dosage, concentration of adsorbate, and contact time.

2. Materials and Methods

2.1. Chemicals and Reagents. The rice husk ash was collected from the brick-kiln industry (Tra Vinh Province, Vietnam). Hydrochloric acid (HCl, 98%), sodium hydroxide (NaOH), sulfuric acid (H₂SO₄, 98%), sodium salicylate (C₇H₆NaO₃, 99.5%), postassium nitrate (KNO₃, 99%), and postassium sodium tartrate tetrahydrate (C₄H₄KNaO₆·4H₂O, 99.5%) were purchased from Sigma-Aldrich.

2.2. Extraction Process of SiNPs. SNPs were extracted from RHA based on the sol-gel method. The extraction process could be briefly described: firstly, RHA of 2 g was collected from the brick-kiln industry, then washed with DI water for removal of dirt, and then soaked in the sodium hydroxide solvent (3.5 M) under stirring at the speed of 400 rpm to generate sodium silicate. The RHA-induced sodium silicate filtrated to remove the nonreactive impurities. Finally, the sodium silicate solution obtained was cooled at room temperature and added to hydrochloric acid (4 M) under vigorous stirring in order to initiate the hydrolysis-condensation reaction at pH 7. The gel obtained was then dispersed in ethanol, washed with distilled water (three times), and dried at 110°C for 2 h to remove remaining surfactants. The SNPs synthesized were stored in desiccator for further characterizations [28].

2.3. Adsorption Process for Nitrate Ion Removal. In this study, SiNPs were generated from the rice husk ash based on the sol-gel method [28] and utilized for nitrate removal. An adsorption capacity of nitrate was investigated based on the controllable parameters including contact time, pH, adsorbent’s mass, and concentration at room temperature. In addition, pH was varied from 4 to 8, and contact time changed from 20 to 60 minutes with an increment of 10 min each. Nitrate concentration was set from 5 to 20 mg·L⁻¹, and adsorbent’s mass changed from 0.05 to 0.2 g. The concentration of nitrate ions was analyzed by using a UV-Vis spectrophotometer. The standard nitrate ion was generated by mixing sodium salicylate (0.5 mL), postassium sodium tartrate tetrahydrate (10 mL), and sodium hydroxide (2.5 mL). The capacity of adsorption (q_cap) was estimated based on the following equation [29]:

\[ q_{\text{cap}} = \frac{C_{\text{beg}} - C_{\text{fin}}}{m_{\text{SiNPs}}} V, \]

where \( C_{\text{beg}} \) is the nitrate ions’ initial concentration, \( C_{\text{fin}} \) is the concentration of nitrate ions at the equilibrium state, \( m_{\text{SiNPs}} \) is the adsorbent’s mass, and \( V \) is the adsorbate’s volume.

3. Results and Discussion

SiNPs were generated from rice husk ash, and physicochemical properties were characterized by the Fourier transform infrared spectroscopy (FTIR), scanning electronic microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). The results showed that the adsorption bands were obtained at 1069 and 794 cm⁻¹, which corresponded to the symmetric and asymmetric components of Si-O-Si variation as shown in Figure 1(a) [28]. The irregular shapes of SiNPs with a diameter of around 50 nm were achieved by SEM as depicted in Figure 1(b). In addition, the main elements were comprising of Si, O, and Na (Figure 1(c)) with weight concentrations of 23, 75, and 2%, respectively. The small amount of Na remained was due to unperfect process of washing. A combined analysis to determine material-specific surface, pore size distribution, total pore area, and total pore volume (BET and BJH analysis) indicated that SiNPs possessed a surface area of 36 m²g⁻¹ and an averaged pore size of 2.72 nm (Figure 1(d)), leading to considerate that this material may provide a potential application for nitrate elimination.

The capacity of adsorption (mg·g⁻¹) for nitrate ion removal based on SiNPs was studied by investigating the influence of pH, adsorbent mass, and contact time. It was noted that the stirring velocity of 400 rpm and initial concentration of nitrate ions of 20 ppm were remained during the experimental process. It should be noted that each data point in Figures 2(a) and 2(b) and Figure 3 is represented by the mean value of three experimental results. As seen in Figure 2(a), the capability of adsorption reached a maximum value of 4.95 mg·g⁻¹ at pH 6, while the capability of adsorption dropped down when pH value was higher or lower than 6. At pH < 6, Figure 2(a) also presents a low adsorption capability due to chemical decomposition of NO₃⁻ in the form of N₂O. For pH > 6, the loss of NO₃⁻ was caused by the decomposition of NO₃⁻ in the form of N₂ and to a lesser extent of N₂O [30]. When the pH of the aqueous solution increased or decreased, the chemical transformation of NO₃⁻ may prevent the adsorption of nitrate. This leads to obtain more significant capacity of absorption at pH 6.

Table 1 represents the kinetic parameters for nitrate elimination. The fitting equation \( P = P_0 + Ax + Bx^2 \) with parabolic shape was used to fit the experimental data obtained based on the investigation of pH (Figure 2(a)), mass of SiNPs (Figure 2(b)), and contact time (Figure 3) throughout the adsorption process [29]. The fitting results showed that the lowest capacity of adsorption (\( P_0 \)) was 1.19 mg·g⁻¹ for pH change, 4.0 mg·g⁻¹ for mass of SiNPs change, and 4.81 mg·g⁻¹ for contact time change as depicted in Table 1. In the case of pH, the capacity of adsorption obtained was 4 times lower than that of other cases (mass and contact time). This may rely on the chemical transformation of NO₃⁻ as mentioned above. Additionally, the equation was fitted well with the experimental data, due to its large correlation coefficients (\( R^2 \)).

The adsorption kinetics of nitrate ions based on SiNPs were investigated. Figure 3 presents that the optimizing adsorption capacity of 4.96 mg·g⁻¹ was obtained with the
optimized conditions including a SiNP mass of 0.15 g and contact time of 50 min. The nitrate ions were adsorbed by SiNPs and got a saturation at 50 min. The longer time of adsorption was achieved due to the low initial adsorption rate of around 0.244 (mg·min⁻¹). It is noted that the lower the initial adsorption rate is, the longer the equilibrium time is. This relatively low adsorption rate can be attributed to weak diffusion of nitrate ions from surface adsorption sites.
to the bulk SiNP pore, mainly caused by the small pore size of 2.71 nm. Moreover, the adsorption kinetics were studied based on the pseudo-first-order kinetic model (equation (2)) and the pseudo-second-order kinetic model (equation (3)) as follows [30]:

\[
Pt = P_{ad} \left( 1 - e^{-L_1 t} \right),
\]

(2)

\[
Pt = \frac{t}{\left( \frac{1}{L_2 P_{ad}} \right) + \left( t/P_{ad} \right)}
\]

(3)

where \( P_{ad} \) and \( P_t \) were the capacity of adsorption at the saturation time and \( t \), respectively. \( L_1 \) and \( L_2 \) were the first and second pseudo-order rate constants, respectively. The first and second pseudokinetic models represented the kinetics of the solid-liquid system based on adsorption of mononuclear and binuclear, respectively. Table 2 represents the adsorption parameters achieved based on the kinetic equations, while the comparison between the fitting equation and two pseudomodels is revealed in Figure 3. The capacity of adsorption was estimated around 5.0 mg g\(^{-1}\) as seen in Table 2. This result was comparable for both models including the first and second pseudokinetic models and the parabolic one, indicating that three models fitted well into the experimental data. However, the correlation coefficient \( R^2 \) for the case of the parabolic fitting was higher than that of others (the first and second pseudokinetic models), indicating that the parabolic model was more suitable for prediction model of nitrate adsorption.

Our next step is to design adsorption system and adsorption isotherm models for the prediction procedures. Besides, the capacity of adsorption was proved to be also affected by the amount of adsorbent. In this investigation, the nitrate concentration was changed from 5 to 25 mg L\(^{-1}\) with experimental conditions optimized at SiNP mass of 0.15 g, pH 6, and contact time 50 min. The Langmuir (equation (4)) and Freundlich (equation (5)) models were utilized to analyze the data [31]:

\[
C_{eq} = \frac{P_{eq}}{E_L \left( P_{max} - P_{eq} \right)},
\]

(4)

\[
\log P_{eq} = I \log C_{eq} + \log E_F,
\]

(5)

where \( C_{eq}, P_{eq}, \) and \( P_{max} \) were the concentration of nitrate ion, the capacity of adsorption at saturated state, and the maximum capacity of adsorption, respectively; \( E_L \) was the adsorption energy; \( I \) was the intensity of the adsorption; and \( E_F \) was the affinity of adsorption. As shown in Table 3, the affinity between SiNPs and nitrate ions was estimated around 4.85 L mg\(^{-1}\) exhibited strong interaction between nitrate ions and SiNP surface. Especially, the larger the \( E_L \) is, the stronger the affinity of nitrate ions on the surface of SiNPs is. In addition, the adsorption intensity of \( I \) of 0.75 was obtained based on the Freundlich model (Figure 4(b)). This intensity value was lower than 1, resulted in low speed in adsorption of nitrate ions as discussed above [29]. Unlike the Freundlich isotherm, the Langmuir isotherm was an empirical model which implied a maximum adsorption
capacity of the adsorbent. The Langmuir isotherm analysis in Figure 4(a) exhibited a maximum adsorption capacity of 14.22 mg·g⁻¹, indicating that the ability to adsorb nitrate ions of SiNPs was an effective method to discard nitrate from waste-water.

4. Conclusions

In conclusion, the nitrate ions can be removed from aqueous solution by SiNPs extracted from rick husk ash. The amount of nitrate removed and the removal effect will depend on various factors such as pH, mass of adsorbent, concentration of adsorbate, and contact time. The experimental results showed that the maximum adsorption capacity of 14.22 mg SiNPs/g nitrate ions was achieved at pH 6, SiNP mass of 0.15 g, and contact time of 50 min. The capacity of adsorption can be enhanced by the modification of the SiNP surface with functional groups. In addition, the utilization of SiNPs for removal of nitrate ions not only provides an ease-of-use method, but also low cost adsorbent.

Data Availability

This data used to support the findings of this study are available from the corresponding author upon request.

Table 2: Adsorption coefficients for kinetic models.

<table>
<thead>
<tr>
<th>Possible capacity of adsorption Pₐd (mg·g⁻¹)</th>
<th>Kinetic coefficients</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order kinetic model</td>
<td>4.95</td>
<td>0.22</td>
</tr>
<tr>
<td>Pseudo-second-order kinetic model</td>
<td>5.0</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Table 3: Adsorption isotherm parameters for nitrate ion removal.

<table>
<thead>
<tr>
<th>Maximum adsorption capacity Pₘₐₓ (mg·g⁻¹)</th>
<th>Isotherm coefficients</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich isotherm</td>
<td>0.49</td>
<td>0.75</td>
</tr>
<tr>
<td>Langmuir isotherm</td>
<td>14.22</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4: Langmuir isotherm model (a) and Freundlich isotherm model (b) for nitrate ion removal by SiNPs.

Conflicts of Interest

The authors declare no conflicts of interest regarding this work.

Acknowledgments

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