Research Article

Effective Removal of Phosphate from Waste Water Based on Silica Nanoparticles

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1. Introduction

Nowadays, using a lot of fertilizer has caused the release of nutrients, such as phosphorus and nitrogen, from agriculture and aquaculture fields to aquatic systems [1–3]. Leaching of nutrients may lead to many problems such as acceleration of soil acidification and especially to the environmental health [4, 5]. An increase in the amount of phosphate may be associated with the increment of aquatic organism that caused water eutrophication [3, 6–8]. An option to remove phosphate leaching has been reported including biological, chemical, and physical treatment methods such as bioreactor system [9, 10], electrochemical reaction [11, 12], electrodialysis [13, 14], wetland treatment system [15, 16], and anion exchange ion [17–21]. In addition, many physical techniques have been developed to remove phosphate from aqueous solution such as reverse osmosis, ion exchange, electrodialysis, and adsorption. Among these, physical adsorption methods have been studied and widely used for the removal of phosphate ions due to their benefits, i.e., high capacity of adsorption, ease-of-use, low cost, and environmental friendly methods [22–25]. In addition, several promising materials have been used for phosphate removal such as red mud [26], calcium carbonate [27], activated alumina [28], calcium kaolinite [29], soil, fly ash, and coal slag [30–32]. However, these methods have inherent drawbacks such as difficult to maintain biological process at optimum condition, being complicated in operation, high cost, and time-consuming methods. Moreover, these materials required pretreatment for the removal process. It is worth to mention that silica nanoparticles (SiNPs) are promising materials for the removal of phosphate with its high adsorption capacity. Vietnam, the second largest producer of rice in the world, produces about 43.86 billion kilogram a year. In addition, the rice husk ash (RHA), which is contained high amount of silica (approximately 90%), is by-product of a brick-kiln industry. So, the reuse and recycling process of RHA for extraction of SiNPs is cost-effective and environmental friendly method.

The object of the present study was to evaluate the potential of SiNPs extracted from rice husk ash for phosphate removal from an aqueous solution. The physicochemical property of the SiNPs was investigated, and the adsorption conditions were optimized based on several
factors including pH, adsorbent dosage, contact time, and concentration of adsorbate. Adsorption isotherms were also studied at different concentration of phosphate.

2. Materials and Methods

2.1. Reagents. The rice husk ash was taken from brick-kiln industry (Tra Vinh Province, Vietnam). Chemical agents including sodium hydroxide (NaOH), sulfuric acid (H₂SO₄, 98%), hydrochloric (HCl, 98%), potassium phosphate monobasic (KH₂PO₄, 99%), potassium antimony tartrate hemidrstate (K(SbO)C₄H₄O₆·1/2H₂O, 99.5%), acid ascorbic (C₆H₇O₆, 99%), and ammonium molybdate tetrahydrate ((NH₄)₆Mo7O₂4·4H₂O, 99.98%) were purchased from Sigma-Aldrich.

2.2. Preparation of SiO₂ Nanoparticles. SiO₂ NPs were synthesis based on RHA with sol-gel method. The extraction process has been studied and found in the literature [33]. In this work, this could be briefly described with four steps as illustrated in Figure 1. For the first step, RHA (2g) was taken from brick-kiln industry and washed three times for removing dirt under DI water (Figure 1(a)). Then, the sodium silicate was generated by using collected RHA that was put in the NaOH solution (v/v concentration of 3.5 M) with the stirring speed of 400 rpm. The mixture was then filtrated to carry off the nonreactive impurities (Figure 1(b)). The concentration of 4 M (HCl) was added to the obtained sodium silicate solution under vigorous stirring in order to initiate the hydrolysis-condensation reaction at pH~7 (Figure 1(c)). The obtained gel was dispersed in ethanol and washed three times with DI water. Then, the gel was dried at 110°C for 2 h. The synthesized SiO₂ NPs was stored in desiccator for future use.

2.3. Adsorption Process for the Removal of Phosphate. In this work, the phosphate adsorption capacity of SiNPs was studied with various factors at room temperature. The concentration of phosphate was set from 0.5 to 2.5 mg·L⁻¹ and was measured by stannous chloride method, monitoring the absorbance at 690 nm on UV-Vis spectrometer [31]. The effect of pH was investigated in the range 5–9 by controlling the pH of phosphate solution utilizing NaOH and HCl solutions and was measured utilizing pH meter (pH Meter 7110 SET, WTW). The contact time was changed from 30 to 150 min. The effect of adsorbent dosage was studied with different adsorbent dosages from 0.1 to 0.5 g with an increment of 0.1 g. The adsorption experiments were carried out with a stirring speed of 200 rpm at room temperature. The phosphate adsorption capacity (qAC) was estimated by using the equation below [30]:

\[ q_{AC} = \frac{C_{in} - C_{fn}}{m_{SiNPs}}, \]

where \( C_{in} \) is the concentration of phosphate ion at the initial state, \( C_{fn} \) is the concentration of phosphate ions at the equilibrium state, \( m_{SiNPs} \) is adsorbent’s mass, and \( V \) is the adsorbate’s volume.

2.4. Physicochemical and Morphological Characterization. The physicochemical characterization of SiNPs and adsorption of phosphate ions was obtained based on several analytical techniques: Transmission Electron Microscopy (TEM, Keyence VKX-1000) for ultrastructural analysis; Fourier Transform Infrared Spectroscopy (FTIR, Thermo Scientific Nicolet iS50) for determination of functional groups in a range 4000–500 cm⁻¹; Energy Dispersive X-ray Spectroscopy (EDS) for the elemental composition of SiO₂ extracted; Ultraviolet-Visible Spectroscopy (UV-Vis, Shimazu UV-2600) for measurement of concentration of phosphate solution; pore size distribution obtained by BJH (Micrometrics ASAP 2010); surface area measured by the BET method.

3. Results and Discussion

3.1. Characterization of SiNPs. In this work, SiNPs were extracted from rice husk and physicochemical properties were then analyzed by the Transmission Electronic Microscopy (TEM) for ultrastructural analysis, the Fourier Transform Infrared Spectroscopy (FTIR) for determination of functional groups in a range of 500-4000 cm⁻¹, and Energy Dispersive X-ray Spectroscopy (EDS) for composition analysis. Pore size distribution obtained by BJH and surface are measured by the BET method. The results of FTIR analysis represented that the adsorption peaks were achieved at 794 cm⁻¹, 956 cm⁻¹, and 1069 cm⁻¹, which are due to the asymmetric, symmetric, and bending modes of SiNPs, respectively, as shown in Figure 2(a). A TEM micrograph of SiNPs (Figure 2(b)) illustrated that the formed SiNPs were aggregated and the size ranged from a few nanometers to several hundred nanometers. In addition, analyzing the curves in Table 1 can carry out some light on the purities of SiO₂ extracted. The SiNPs extracted contained Si and O, which are compositions of 28.22 and 50.82%, respectively. The remaining of impurities (Na, Al, and K) was due to unperfect washing process. Moreover, BET and BJH analysis showed that SiNPs proposed a specific surface area of 15.56 m²·g⁻¹ with an average pore size of 4.06 nm, leading to provide potential materials for removal of phosphate.

3.2. Effect of Initial Solution pH. To investigate the adsorption behavior of a phosphate ion, all adsorption experiments were performed based on batchwise method to investigate the influence of pH, adsorbent mass, and contact time. Experiments to study the effect of pH were carried out as follows: 0.2 g of adsorbent was added to 50 cm³ of 2 mg·L⁻¹ aqueous sodium phosphate solution, and then the mixture solution was stirred at a speed of 200 rpm at 300 K. It should be noted that each data point in Figures 3 and 4 are represented by the mean value of three experimental results. As shown in Figure 3, the phosphate adsorption capacity was associated with pH value. When pH increased, the adsorption capacity increased. The maximum value was achieved around 4.8 mg·g⁻¹ at pH 7. The phosphate adsorption capacity was dropped down when pH value was
Figure 1: The SiO₂ extraction process. Note. (a) Rice husk ash; (b) filtering solution from rice husk ash diluted in sodium hydroxide; (c) precipitation by acid; (d) SiO₂ powder.

Figure 2: SiNPs characterization. Fourier transform infrared spectrum (a); TEM image (b).
lower or higher than 7. The adsorption phenomena could be explained based on the surface charge of SiNPs. In this case, the experiments were conducted to measure the pH at the potential of zero point charge (pHpzc) based on the pH drift method as shown in Figure 5. The initial pH was set in the pH range of 2 to 12 with an increment of 2 pH unit. Then, the SiNPs of 100 mg was added into the solution for 24 h at a stirring speed of 200 rpm. The experimental results showed that the pHpzc of SiNPs obtained was around 8.7. The SiNPs has a negative surface charge at pH < 7 and positive surface charge at pH > 8. The adsorption behavior of SiNPs surface could be explained based on the competition of three different charges, i.e., H⁺, OH⁻, and PO₄³⁻ of the surrounding medium at pH < 7 or at pH > 8. This indicates that phosphate ions were physically adsorbed on the surface of SiNPs through the pore capillaries at the optimizing 7 < pH < 8.7, which corresponds to pHpzc of SiNPs. The pH increased or decreased, the salinity may prevent phosphate adsorption by Al oxide by making deformation of phosphate from H₂PO₄⁻ to HPO₄²⁻ and by a change to the surface charge of the oxide mentioned [34].

3.3. Effect of SiNPs Dosage. In this work, the parabolic shape curve with a quadratic second order equation \( q = q_0 + ax + bx^2 \) was used to fit to the experimental data presented in Figures 3, 4, and 6 [30]. This is to find an ideal characteristic shape for removing phosphate with various parameters, i.e., pH, mass, and contact time. The analyzed results showed that the minimum adsorption capacity of phosphate (\( q_0 \)) based on SiNPs was 0.8 mg·g⁻¹ for pH change (Figure 3), 4.98 mg·g⁻¹ for SiNPs dosage change (Figure 4), and 4.47 mg·g⁻¹ for adsorption time change (Figure 6), respectively. The fitting results also illustrated that, in the
case of pH, the minimum possible adsorption capacity drops to a value 6 times lower than in the other cases. This was caused by the deformation of phosphate ion from $\text{H}_2\text{PO}_4^-$ to $\text{HPO}_4^{2-}$, SiNPs surface charge, as discussed above. In addition, all of the correlation coefficients ($R^2$) for three different cases including effect of pH, effect of mass, and change of adsorption time were higher than 0.70 as shown in Table 2. This indicated that the model proposed, i.e., the quadratic second order equation, fitted well into the experimental data.

### 3.4. Adsorption Isotherm and Their Modelling

Furthermore, Figure 6 represents the adsorption kinetics of SiNPs extracted. The figure showed the adsorption capacity of 5.2 mg g$^-1$ with the optimized conditions, i.e., adsorption time of 90 min with a SiNPs loading mass of 0.3 g. Figure 6 shows that the phosphate ions were slowly adsorbed by SiNPs and achieved a plateau value at 90 min. Moreover, the initial adsorption rate of 0.12 mg g$^-1$ min$^-1$ was achieved based on the experimental data. It is worth mentioning that the lower the adsorption rate is, the shorter the plateau time is. This relatively low adsorption rate of SiNPs can be contributed to the weak diffusion of phosphate ions from surface adsorption sites to the bulk SiNPs pore, which is mainly caused by the small pore size of 4.06 nm. In addition, the adsorption kinetics was investigated by utilizing the pseudo-first-order kinetic model (Equation (2)) and the pseudo-second-order kinetic model (Equation (3)) as given below [35, 36]:

$$q_t = q_{ad}(1 - e^{-P_1t}), \quad (2)$$

$$q_t = \frac{t}{(1/P_2q_{ad}) + (t/q_{ad})}, \quad (3)$$

where $q_{ad}$ and $q_t$ were the adsorption capacities of phosphate at the plateau time and $t$, respectively. $P_1$ and $P_2$ were the pseudo-first- and the pseudo-second-order rate constants, respectively. It should be noted that the first pseudo kinetic model and the second ones represented the kinetic adsorption of mononuclear and binuclear of the solid-liquid system, respectively. Table 3 presents the adsorption coefficients that were achieved based on those above equations. In addition, Figure 6 presented a comparison between the parabolic model and the two pseudo kinetic models. The phosphate adsorption capacity was estimated around 5.0 mg g$^-1$ as presented in Table 3. This value agrees with the experimental results. Moreover, the correlation coefficient ($R^2$) was obtained around 0.74; 0.55; 0.92 for the case of the parabolic model, the pseudo-first-kinetic model, and the pseudo-second-kinetic model, respectively. These results indicated that the phosphate adsorption system studied belongs to the pseudo-second-kinetic model.

The models of adsorption isotherm are important for the prediction of the adsorption process to design the adsorption system. Normally, the adsorption capacity could be estimated based on choosing the approximate dosage of absorbent. In this work, the phosphate concentration was set in the range of 0.5 to 2.5 mg L$^-1$. Then, the experiment was performed based on the optimum parameters, i.e., pH 7, SiNPs dosage of 0.3 g, and adsorption time of 90 min at room temperature. Then, the Langmuir (Equation (4)) and Freundlich (Equation (5)) models were applied to analyze the experimental data, respectively [35, 37].

$$C_{eq} = \frac{q_{eq}}{A L (q_{max} - q_{eq})}, \quad (4)$$

$$\log q_{eq} = I \log C_{eq} + \log A_F, \quad (5)$$

where $C_{eq}$, $q_{eq}$, and $q_{max}$ were the phosphate concentration, the adsorption capacity of phosphate at the equilibrium state, and the maximum adsorption capacity of phosphate, respectively; $A_L$ was the adsorption energy; $I$ was the adsorption intensity; $A_F$ was the adsorption affinity.

The fitting parameters, i.e., the adsorption factors and the correlation coefficients, were obtained based on the Langmuir (Figure 7(a)) and Freundlich (Figure 7(b)) models as illustrated in Table 4. The adsorption intensity ($I$) of 0.34, which was estimated utilizing the Freundlich model, was smaller than one that represented a low adsorption rate of the phosphate ions. This leads to the long adsorption time of 90 min as mentioned in Figure 6. In Table 4, the affinity between adsorbent and phosphate ions was estimated at around 0.69 mg g$^-1$ offered weak interaction between SiNPs

### Table 2: Kinetic coefficients for removing phosphate.

<table>
<thead>
<tr>
<th>Minimum capacity of adsorption $q_e$ (mg g$^-1$)</th>
<th>Fitting parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>$a$ (a.u.)</td>
</tr>
<tr>
<td>4.47</td>
<td>0.04</td>
</tr>
<tr>
<td>Mass</td>
<td>4.98</td>
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<td>pH</td>
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### Table 3: Adsorption coefficients for kinetic models.

<table>
<thead>
<tr>
<th>Possible adsorption capacity $q_{ad}$ (mg g$^-1$)</th>
<th>Kinetic coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order model</td>
<td>$P_1$ (min$^-1$)</td>
</tr>
<tr>
<td>4.89</td>
<td>0.04</td>
</tr>
<tr>
<td>Pseudo-second-order model</td>
<td>—</td>
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</table>


surface and phosphate ions. It should be noted that the larger $A_L$ values produced the higher adsorption of phosphate in an approximately linear fashion. This result was given agreement with the low initial adsorption rate of 0.12 mg·g$^{-1}$·min$^{-1}$ as mentioned above. Unlike the Freundlich isotherm model, the Langmuir isotherm model was a practical model which proposed a maximum adsorption capacity of the phosphate. In Figure 7(b), the Langmuir isotherm model exhibited a maximum adsorption capacity of 9.08 mg·g$^{-1}$, which is higher compared to the research found in the literature as depicted in Table 5. In addition, the Langmuir isotherm described a better fit using the experimental data based on correlation coefficient ($R^2$), which was higher than that of Freundlich isotherm. This leads us to believe that SiNPs can be applied to remove phosphate from waste water as an effective method.

3.5. Comparison of SiNPs with Other Absorbents. Table 5 presents the phosphate ion adsorption of SiNPs and other materials including fly ash, steel slag, and red mud. It can be observed that the maximum adsorption capacity of SiNPs is better than that of other adsorbents under similar experimental condition. Therefore, the use of SiNPs for the adsorption of phosphate is a friendly and cost-effective method. In addition, the use of SiNPs may offer several benefits for the adsorption of heavy metals based on conjugation with various functional groups for specific detection such as heavy metal ions (Pb$^{2+}$, Cu$^{2+}$, Cr$^{6+}$), for environmental applications.

4. Conclusions

In conclusion, this study investigated the ability of SiNPs extracted from rice husk ash to adsorb phosphate from aqueous solution under various parameters, i.e., mass of adsorbent, pH, adsorbate concentration, and adsorption time. The experimental results showed that the maximum adsorption capacity of 9.08 mg SiNPs g$^{-1}$ phosphate was obtained at pH 7, SiNPs dosage of 0.3 g, and adsorption time of 90 min. The phosphate adsorption capacity can be enhanced by the surface modification of the SiNPs with functional groups. In addition, the use of SiNPs for removing phosphate ions not only offers an ease-of-use method and high efficient but also low cost of adsorbents.
Data Availability
This data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

Acknowledgments
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References


