Recovery Technique for Phosphate Using Granular Gibbsite with Binder

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ABSTRACT
In the present study, granular gibbsite with vinyl acetate (20%, G-GB20) was used for the removal of phosphate from artificial sewage. The amount of phosphate adsorbed was studied using batch techniques. The effect of different parameters, namely contact time, initial concentration, solution pH, and temperature were investigated. The adsorption kinetics data were best described by the pseudo-second-order rate equation and equilibrium was achieved after 12 h. The Langmuir and Freundlich equations for describing adsorption equilibrium were applied to the experimental data. The correlation coefficients of the Langmuir and Freundlich equations were 0.960 - 0.996 and 0.960 - 0.995, respectively. A number of thermodynamic parameters, namely free energy, enthalpy, and entropy change for the adsorption of phosphate were evaluated and it was found that the reaction was spontaneous and endothermic in nature. Adsorbent (G-GB20) was used for repeated adsorption and desorption of phosphate and a breakthrough curve was obtained. It was shown that G-GB20 could be used three times for repetitive adsorption and desorption of phosphate. Results suggest that the prepared G-GB20 has great potential in the remediation of water contaminated by phosphate.

Keywords: adsorption, artificial sewage, granulation, phosphate, vinyl acetate

INTRODUCTION
Phosphorus (as phosphate ions) is an essential nutrient in aquatic environments (Nijboer and Verdonschot, 2004). Phosphorus and nitrogen are important elements that are widely used in agriculture as fertilizers and in industries as detergents. However, their use poses many problems, notably eutrophication, when they are released into aquatic environments (Meyer-Reil and Koster, 2000). Algal blooms due to phosphate run off in coastal areas cause huge economic damage (Ruan and Gilkes, 2000). In many countries, stringent regulations limit phosphorus levels to 0.05 mg/L to prevent increased algal growth (Behrendt et al., 1997).

Phosphate is an exhaustible resource and Japan depends solely on imports owing to a lack of rock phosphate. Regulation of exports by the USA and China has pushed up the price of this resource over time, producing a great need for the development of methods to recycle it. Of the 0.7 million tons of phosphate imported per year by Japan, 25 tons are disposed (Ohtake, 2011).

The concentration of phosphate in environmental water is very low. Moreover, the recovery of phosphate from environmental water is difficult because no useful and effective recovery technology for low levels of phosphate currently exists. Various techniques have been developed for the removal of phosphate from water and wastewater (Duenas et al., 2003), which include chemical precipitation (Ruixia et al., 2002), adsorption using suitable materials (Chitrakar et al., 2006a), biological treatment
(Gieseke et al., 2002), and crystallization (Eggers et al., 1991). Adsorption is a comparatively useful and economical method for phosphate removal. Many types of adsorbents have been investigated, including a synthetic hydrotalcite (Kuzawa et al., 2006), powder freshwater mussel shells (Xiong et al., 2011), wheat straw (Ma et al., 2011), low cost aleppo pine adsorbent (Benyoucef and Amrani, 2011), iron and aluminum hydroxyl coated filter media (Ayoub et al., 2011), red mud (Huang et al., 2008), kaolinite (Kamiyango et al., 2009), and crab shells (Jeon and Yeom, 2009).

Although the concentration of phosphate in environmental water is very low, its concentration in sewage is very high owing to phosphate excretion by humans. Therefore, recovery of phosphate from sewage is very important and useful for sustainable development. Recovery of phosphate from sewage has been widely reported (Guney et al., 2008; Blocher et al., 2012). However, removal of phosphate using adsorbent granulated with binder (vinyl acetate) has not been reported to date and this work aims to address this issue.

In the present study, gibbsite (GB, aluminum hydroxide) was used as an adsorbent for the removal of phosphate from artificial sewage. Moreover, GB was granulated with binder to increase the particle diameter. The effects of various operating conditions on phosphate removal were investigated. Granulation conditions of GB, characteristics of granular GB, adsorption isotherms, contact time, temperature and solution pH on sorption process, repetition of adsorption and desorption, and breakthrough curves were all assessed.

MATERIALS AND METHODS

Materials
Gibbsite (GBH42-M, aluminum hydroxide) was purchased from Showa Denko, Japan. It was composed of adhesive moisture (0.23%), Al(OH)₃ (99.6%), Fe₂O₃ (0.01%), SiO₂ (0.01%), Na₂O (0.03%), and ω-Na₂O (0.05%). The mean particle size, bulk density, specific surface area, moisture adsorption capacity, and the amount of surface hydroxyl group of GB were 1.1 µm, 0.2 - 0.5 g/cm³, 5.0 m²/g, 0.90%, and 4.23 mmol/g, respectively.

Calcined GB was prepared by treating 20 g of virgin GB in a muffle furnace with a temperature of 200 - 1,000°C (GB200-GB1000) for 2 h. Granular GB was prepared by adding vinyl acetate to the GB400 and mixing, followed by drying for 24 h (GB400 containing about 15%, 20%, and 25% vinyl acetate were named as G-GB15, G-GB20, and G-GB25, respectively). The particle diameter was 500 - 840 µm.

Thermogravimetric-differential thermal analysis (TG-DTA) was carried out using a DTG-60AH (Shimadzu, Japan), scanning electron microscopy (SEM) was carried out using a JSM-5500LV (JEOL, Japan), specific surface area was measured using a FlowSorb II 2300 (Micromeritics, Japan), and the amount of surface hydroxyl groups were measured using the method of fluoride ion adsorption (Boehm, 1966). The pH of a solution was measured using a digital pH meter (Mettler-Toledo International Inc., Japan).
Artificial sewage consisted of CaCl₂·2H₂O (50 mg/L), MgSO₄·7H₂O (236 mg/L), NaCl (100 mg/L), NaHCO₃ (150 mg/L), NaH₂PO₄·2H₂O (32 mg/L), (NH₄)₂SO₄ (70 mg/L), D-glucose (50 mg/L), and peptone (210 mg/L) (Yamaguchi et al., 2005).

Amount of phosphate adsorbed
After adding 0.05 g of adsorbents (Virgin GB, GB200, GB400, GB600, GB800 and GB1000) to 50 mL of artificial sewage solution at different phosphate concentrations, the suspension was shaken at 100 rpm for 24 h at 25°C. The concentration of phosphate after filtration using a 0.45 µm membrane filter was measured by the ascorbic acid method using PhosVer® 3 Phosphate Reagent Powder Pillows (Hach, USA). The amount of phosphate adsorbed was calculated using equation (1),

\[ q = \frac{(C_0 - C_e)V}{W} \]  

where \( q \) is the amount of phosphate adsorbed in mg/g, \( C_0 \) is the initial phosphate concentration in mg/L, \( C_e \) is the equilibrium phosphate concentration in mg/L, \( V \) is the solvent volume in L, and \( W \) is the weight of adsorbent in g.

Screening test for phosphate adsorption in artificial sewage solutions
After adding 0.05 g of adsorbents (G-GB15, G-GB20, G-GB25, and vinyl acetate) to 50 mL of artificial sewage containing 19.7 mg/L of phosphate solution, the suspension was shaken at 100 rpm for 24 h at 25°C. The amount of phosphate adsorbed was calculated using equation (1). Moreover, after adding 0.05 g of G-GB20 to 50 mL of artificial sewage solution at different phosphate concentrations, the suspension was shaken at 100 rpm for 24 h at 15 - 35°C.

Effect of contact time and solution pH on phosphate adsorption onto G-GB20
After adding 0.05 g of G-GB20 to 50 mL of artificial sewage containing 30 mg/L of phosphate solution, the suspension was shaken at 100 rpm for 1 - 24 h at 25°C. A sample of solution was collected at the end of each time interval and filtered using a 0.45 µm membrane filter. The amount of phosphate adsorbed onto G-GB20 was calculated using equation (1).

After adding 0.05 g of G-GB20 was added to 50 mL of artificial sewage containing 30 mg/L of phosphate solution with pH values ranging from 2.0 to 7.0. The amount of phosphate adsorbed was then measured by the aforementioned procedure.

Amount of phosphate adsorbed onto and desorbed from G-GB20 with NaOH
After adding 0.5 g G-GB20 was added to 200 mL of artificial sewage containing 60 mg/L of phosphate solution, and the suspension was shaken at 100 rpm for 24 h at 25°C. The amount of phosphate adsorbed was then calculated using equation (1). The G-GB20 was collected after the adsorption step and then dried at room temperature. It was then added to 300 mL of sodium hydroxide solution at different concentrations (1 mmol/L, 5 mmol/L, and 10 mmol/L), and the suspension was shaken at 100 rpm for 24 h at 25°C. The solution was filtered using a 0.45 µm membrane filter, and subsequently the amount of phosphate desorbed was calculated using equation (2).

\[ d = \frac{C_eV}{W} \]  

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where $d$ is the amount of phosphate desorbed in mg/g, $C_e$ is the equilibrium phosphate concentration in mg/L, $V$ is the solvent volume in L, and $W$ is the weight of adsorbent in g.

These adsorption and desorption steps were repeated three times. In addition to this, the concentration of aluminum ions released from G-GB20 was measured by an adsorption spectrophotometric method (DR/890, HACH, USA).

**Breakthrough curve of phosphate adsorption onto G-GB20**

The amount of phosphate adsorbed onto a column (1 cm diameter by 10 cm height) was measured. Approximate conditions for the column experiment were as follows: Condition 1 - initial concentration of phosphate, 33.4 mg/L; space velocity (S.V.), 15.6 h$^{-1}$; linear velocity (L.V.), 0.78 m/h; flow rate, 1.0 mL/min; weight of adsorbent, 3.07 g; filling height, 5.0 cm; adsorption time, 40 h and desorption time, 3 h. Condition 2 - initial concentration of phosphate, 29.6 mg/L; space velocity (S.V.), 7.7 h$^{-1}$; linear velocity (L.V.), 0.46 m/h; flow rate, 0.6 mL/min; weight of adsorbent, 2.53 g; filling height, 6.0 cm; adsorption time, 80 h and desorption time, 3 h. The amount of phosphate adsorbed was calculated as the difference between the initial concentration and the released concentration from the column. After adsorption, desorption process was investigated. Sodium hydroxide (1 mmol/L) was used as the desorption solution.

**RESULTS AND DISCUSSION**

**Adsorption isotherms of phosphate onto GBs**

Adsorption isotherms of phosphate using GBs are shown in Fig. 1. As a result, the amount adsorbed was in the order: virgin GB $\approx$ GB200 $<$ GB800 $\approx$ GB1000 $<$ GB600 $<$ GB400. We previously reported that the specific surface area and the amount of hydroxyl groups of GB400 were greater than that of other GBs (Ogata et al., 2009), which suggested that the amount of phosphate adsorbed onto GB400 would also be greater than that adsorbed onto other GBs (Specific surface area or surface hydroxyl groups of virgin GB, GB200, GB400, GB600, GB800 and GB1000 were 4.2, 4.6, 295.3, 176.1, 128.1 and 36.8 m$^2$/g or 2.7, 2.8, 5.0, 4.6, 3.8 and 1.0 mmol/g, respectively.). We previously reported that the amount of phosphate adsorbed is based on specific surface area and surface hydroxyl groups. The amount of phosphate adsorbed onto GB in distilled water was greater than that absorbed onto GB in the artificial sewage solution (Ogata et al., 2009), which indicated that the components of the artificial sewage solution affected the adsorption of phosphate. Based on these results, we selected GB400 for subsequent granulation with binder.

**Optimal conditions for granulation of GB400**

The amount of phosphate adsorbed onto G-GBs and vinyl acetate binder are shown in Fig. 2. The amount adsorbed was in the order: G-GB20 $>$ G-GB25 $>$ G-GB15 $>$ vinyl acetate (binder). Adsorbent (G-GB20) was found to be the best condition after granulation of GB400 with vinyl acetate binder. Moreover, the vinyl acetate binder alone also had the ability of adsorbing phosphate. The amount of phosphate adsorbed onto GB400 was 30.2 mg/g (Kawasaki et al., 2008). The amount of phosphate adsorbed onto G-GB20 was lower than that onto GB400, which indicated that the vinyl acetate binder masked the surface adsorption site onto G-GB20 and inhibited the adsorption of phosphate from aqueous solution.
Characteristics of G-GB20
An SEM image and the results of the TG-DTA of G-GB20 are shown in Figs. 3 and 4, respectively. It can be seen from Figs. 3 and 4 that the GB400 can be granulated with vinyl acetate (binder). The results of the TG-DTA of G-GB20 showed that dehydration of bound water occurred at 320°C. The specific surface area (187.6 m$^2$/g) and surface
hydroxyl groups (0.36 mmol/g) of G-GB20 were decreased compared with the specific surface area (295.3 m²/g) and surface hydroxyl groups (5.0 mmol/g) of GB400 (Ogata et al., 2009). The particle diameter was increased by granulation with the binder, which induced a decrease in the specific surface area and surface hydroxyl groups. It is also possible that the adsorption sites may have been masked by the binder.

Fig. 3 - SEM image of G-GB20.

Fig. 4 - TG-DTA results for G-GB20.
Adsorption isotherms of phosphate onto G-GB20 at different temperatures

The adsorption isotherms of phosphate onto G-GB20 at different temperatures are shown in Fig. 5. The results show that the amount of phosphate adsorbed onto G-GB20 is lower than that of phosphate adsorbed onto GB400. This is attributed to the lower specific surface area and the lesser number of surface hydroxyl groups of G-GB20 compared to that of GB400 as aforementioned. The solution pH was 6.45 - 7.65 after adsorption of phosphate.

The amount of phosphate adsorbed onto G-GB20 was not affected by temperature (Ogata et al., 2009). The equilibrium adsorption isotherms are some of the most important data for understanding the mechanism of adsorption systems. The adsorption process is normally described by the Langmuir and the Freundlich isotherms. The Langmuir equation assumes that adsorption occurs at specific homogenous sites within the adsorbent and has been successfully applied in many studies of monolayer adsorption (Langmuir, 1918). The linear form of the Langmuir equation is written as

$$ q_e = q_m b C_e / (1 + b C_e) $$

where $q_m$ is the monolayer adsorption capacity of the adsorbent in mg/g, $C_e$ is the equilibrium concentration in mg/L, $q_e$ is the amount of phosphate adsorbed in mg/g, and $b$ is the Langmuir adsorption constant in L/mg, which is related to the free energy of adsorption.

The Freundlich equation assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available (Freundlich, 1906). The Freundlich equation is more widely used than the Langmuir equation but provides no information on the monolayer adsorption capacity. Its linearized form can be written as

$$ \log q_e = \log K_1 + \frac{1}{n} \log C_e $$

where $K_1$ and $n$ are the Freundlich adsorption isotherm constants, being indicative of the extent of adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively.

Adsorption equations (Table 1) were obtained from experimental data with equations (3) and (4). The results show that the correlation coefficients of the Langmuir model and Freundlich model are 0.960 - 0.995 and 0.960 - 0.996, respectively. These results indicate that the adsorption data of phosphate using G-GB20 fitted both the Langmuir and the Freundlich models. The Freundlich constant ($1/n$) was 0.46 - 0.66, which suggested that the adsorbate is easily adsorbed (Abe et al., 1976). (When constant $1/n$ is in the range 0.1 - 0.5, the adsorbate is considered to be easily adsorbed. On the other hand, if $1/n > 2$, the adsorption is considered to be difficult.)

Adsorption thermodynamics

The nature and thermodynamic feasibility of the sorption process were determined by evaluating the thermodynamic constants, standard free energy ($\Delta G$), standard enthalpy ($\Delta H$), and standard entropy ($\Delta S$) using equations (5) and (6) (Dore et al., 1986;
\[ \ln \left( \frac{q_e}{C_e} \right) = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \]  

\[ \Delta G = -RT \ln \left( \frac{q_e}{C_e} \right) \]  

The obtained thermodynamic parameters are given in Table 2. The positive value of \( \Delta H \) (mean value of 7.81 kJ/mol) confirms the endothermic nature of the adsorption process (Ruhan et al., 2009). The positive value of \( \Delta S \) (mean value of 30.30 J/mol/K) means an increase in the randomness at the solid/solution interface during the adsorption of phosphate onto G-GB20 (Aziz et al., 2009). The Gibbs free energy change (\( \Delta G \)) was calculated to be -0.48 kJ/mol, -2.15 kJ/mol, and -1.03 kJ/mol for 288 K, 298 K and 308 K.
The negative $\Delta G$ values indicate the spontaneous nature of the adsorption. These values (higher than -20.00 kJ/mol) indicate that electrostatic interactions may play a significant role in the adsorption process. It may be that this is the major mechanism responsible for the phosphate adsorption process (Weng et al., 2007).

**Adsorption rate of phosphate onto G-GB20**

Result (Fig. 6) shows the effect of contact time on the adsorption of phosphate onto G-GB20. For these cases, the equilibrium concentration was reached within 12 h. A simple kinetic analysis of adsorption is the Lagergren’s pseudo-first-order differential equation (Demiral and Gunduzoglu, 2010), which can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_2 t$$  \hspace{1cm} (7)

where $k_2$ is the rate constant of pseudo-first-order adsorption (1/h).

The pseudo-second-order model can be expressed as (Amin, 2008; Alvin et al., 2010)

$$\frac{t}{q_t} = \frac{1}{k_3 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (8)

where $k_3$ is the pseudo-second-order rate constant (g/mg h).

The acquired parameters from the kinetic equations used, with $r$ values, are summarized in Table 3. It can be seen that the correlation coefficients of $r$ pseudo-first-order and pseudo-second-order models are 0.802 and 0.918, respectively. The amount of phosphate adsorbed ($q_e$: 17.9 mg/g) and the correlation coefficient ($r$ value: 0.918) of the pseudo-second-order model were in good agreement with the experimental data. Therefore, it was concluded that phosphate adsorption onto G-GB20 followed the second-order kinetic model.

### Table 2 - Thermodynamic parameters for adsorption of phosphate onto G-GB20.

<table>
<thead>
<tr>
<th>Phosphate concentration (mg/L)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol/K)</th>
<th>$\Delta G$ (kJ/mol) at temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>288K</td>
<td>298K</td>
<td>308K</td>
</tr>
<tr>
<td>3</td>
<td>-10.24</td>
<td>-22.24</td>
<td>-3.00</td>
</tr>
<tr>
<td>9</td>
<td>6.96</td>
<td>29.06</td>
<td>-0.88</td>
</tr>
<tr>
<td>15</td>
<td>22.56</td>
<td>77.51</td>
<td>0.60</td>
</tr>
<tr>
<td>21</td>
<td>13.89</td>
<td>47.62</td>
<td>0.35</td>
</tr>
<tr>
<td>30</td>
<td>5.88</td>
<td>19.54</td>
<td>0.52</td>
</tr>
<tr>
<td>Mean</td>
<td>7.81</td>
<td>30.30</td>
<td>-0.48</td>
</tr>
</tbody>
</table>

308 K, respectively. The negative $\Delta G$ values indicate the spontaneous nature of the adsorption. These values (higher than -20.00 kJ/mol) indicate that electrostatic interactions may play a significant role in the adsorption process. It may be that this is the major mechanism responsible for the phosphate adsorption process (Weng et al., 2007).
Effect of solution pH on phosphate adsorption
The amount of phosphate adsorbed onto G-GB20 at different pH values is shown in Fig. 7. It can be seen that the removal rate increases from 11.8 mg/g to 15.8 mg/g with an increase in pH from 2.55 to 6.45. Thereafter, no significant change is observed for the removal rate from 15.8 mg/g to 14.6 mg/g with an increase in pH from 6.45 to 7.22. These results suggest that the optimum pH for the removal of phosphate adsorbed onto G-GB20 is about 6 – 8. The adsorption was most favored in neutral solution. In the pH range 2.55 – 6.45, the adsorption occurs through an ion-exchange mechanism of phosphate hydrolysis products (H₂PO₄⁻, HPO₄²⁻). Also, high pH caused a decrease in the binding capacity of PO₄³⁻ on the adsorbent surface because of competition with OH⁻ ions (Oguz et al., 2003).

Fig. 6 - Adsorption rate of phosphate onto G-GB20.

Table 3 - Pseudo-first-order and pseudo-second-order constants for phosphate adsorption onto G-GB20.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Model</th>
<th>qₑ (mg/g)</th>
<th>k₂ (h⁻¹) or k₃ (g/mg h)</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-GB20</td>
<td>Pseudo-first-order</td>
<td>11.4</td>
<td>0.327</td>
<td>0.802</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>17.9</td>
<td>0.009</td>
<td>0.918</td>
<td></td>
</tr>
</tbody>
</table>

Effect of solution pH on phosphate adsorption
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Table 4 shows the amounts of phosphate adsorbed and desorbed using G-GB20 with NaOH. As a result, after thrice adsorption of phosphate, G-GB20 exhibited the adsorption and desorption ability of phosphate. These results indicate that G-GB20 could be used three times for repetitive adsorption and desorption of phosphate. Using 1 mmol/L, 5 mmol/L, and 10 mmol/L NaOH, the amount of phosphate adsorbed were 20.1 mg, 21.9 mg, and 26.2 mg, respectively, while the amount of phosphate desorbed were 4.8 mg, 11.7 mg, and 18.1 mg. Moreover, the desorbed percentage of phosphate for the three concentrations of NaOH used 23.7%, 53.4%, and 69.2%, respectively. These results suggest that regeneration of adsorption and desorption ability of G-GB20 using NaOH solution is possible. The amount of phosphate desorbed increased with increasing concentrations of NaOH solution. However, the concentration of aluminum released from G-GB20 also increased. Taking into consideration the specific application of this process, we selected 1 mmol/L NaOH solution for desorption of phosphate to minimize aluminum release. Moreover, comparison of the adsorption capacity of phosphate onto various adsorbents is shown in Table 5 (Seida and Nakano, 2002; Zeng et al., 2004; Chitrakar et al., 2006b; Ogata et al., 2011). The adsorption capacities of phosphate onto GB400 and G-GB20 were 30 mg/g and 12 mg/g, respectively. The adsorption capacity of phosphate onto various adsorbents was in the range 9 - 15 mg/g. Our suggested G-GB20 was efficient for phosphate adsorption and comparable to the previously reported adsorbents.

**Breakthrough curves of phosphate adsorption onto G-GB20**
The breakthrough curves are shown in Fig. 8. It can be seen that phosphate from the column is detected immediately after starting adsorption under Condition 1. On the other hand, phosphate from the column was released 35 h after starting the adsorption.
under Condition 2. Space velocity and L.V. in Condition 1 were greater than those in Condition 2, which suggested that Condition 2 for the adsorption of phosphate with a column was most useful for practice. The amount of phosphate adsorbed, amount desorbed, and desorbed percentage for Conditions 1 and 2 were 61.6 mg, 1.3 mg, and 2.2% and 76.1 mg, 1.3 mg, and 1.7%, respectively. The amount of phosphate desorbed from G-GB20 was very small since desorption time (3 h) using NaOH solution was short. This is an important parameter to control in order to improve the life of the adsorbent.

Table 4 - Amount of phosphate adsorbed and desorbed using G-GB20 with NaOH.

<table>
<thead>
<tr>
<th>Concentration of NaOH (mmol/L)</th>
<th>Cycles (times)</th>
<th>Amount adsorbed (mg/g)</th>
<th>Amount desorbed (mg/g)</th>
<th>Concentration of released Al (mg/L)</th>
<th>Recovery percentage (%)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>1</td>
<td>21.6</td>
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<tr>
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<td>10.4</td>
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<td>3</td>
<td>9.0</td>
<td>4.0</td>
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<tr>
<td>5.0</td>
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<td>21.5</td>
<td>7.4</td>
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</tr>
<tr>
<td></td>
<td>2</td>
<td>8.9</td>
<td>6.8</td>
<td>1.3</td>
<td>29.6</td>
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<tr>
<td></td>
<td>3</td>
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<td>10.1</td>
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<tr>
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<td>10.8</td>
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<td>50.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>16.3</td>
<td>13.1</td>
<td>3.1</td>
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<td></td>
<td>3</td>
<td>16.6</td>
<td>14.7</td>
<td>3.4</td>
<td>48.6</td>
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</table>

Table 5 - Comparison of the adsorption capacity of phosphate onto various adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB400 (powder)</td>
<td>30</td>
<td>This work</td>
</tr>
<tr>
<td>G-GB20 (granulated)</td>
<td>12</td>
<td>This work</td>
</tr>
<tr>
<td>Layered double hydroxides containing iron</td>
<td>10</td>
<td>Seida and Nakano (2002)</td>
</tr>
<tr>
<td>Goethite and akaganeite</td>
<td>9-10</td>
<td>Chitrakar et al. (2006b)</td>
</tr>
<tr>
<td>Iron-loaded tannin gel</td>
<td>15</td>
<td>Ogata et al. (2011)</td>
</tr>
<tr>
<td>Iron oxide tailing</td>
<td>9</td>
<td>Zeng et al. (2004)</td>
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</table>
CONCLUSIONS
The present study found that granular gibbsite can be used as an effective adsorbent for the removal of phosphate from artificial sewage. Gibbsite was granulated with vinyl acetate (G-GB20) and was subsequently shown to be capable of adsorbing phosphate from artificial sewage. Adsorption isotherm data were fitted to the Langmuir and Freundlich equations. From the thermodynamic parameters, the adsorption reaction was seen to be spontaneous and endothermic in nature. The kinetics of sorption followed the pseudo-second-order model. Adsorbent (G-GB20) was useful for the removal of phosphate from artificial sewage with three repetitions possible. The prepared G-GB20 has huge potential for the remediation of phosphate-contaminated water.

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REFERENCES


