Phosphate-Ion-Adsorption Capability of Granulated Boehmite Fabricated Using Organic Binder (Polyethylene Terephthalate)

Fumihiko Ogata, Ayaka Ueda, and Naohito Kawasaki*

Faculty of Pharmacy, Kinki University; 3–4–1 Kowakae, Higashi-Osaka, Osaka 577–8502, Japan.

Received May 20, 2013; accepted July 26, 2013

We investigated a method for producing granulated boehmite (BE) by using an organic binder and measured its phosphate-ion-adsorption capacity. BE was granulated using polyethylene terephthalate (PET), and its structure was characterized by scanning electron microscopy and X-ray diffraction analyses. The properties of granulated BE such as specific surface area, mean pore diameter, pore volume, amount of hydroxyl groups, and solution pH were also investigated. Furthermore, adsorption isotherm; effects of contact time, temperature, and solution pH on phosphate-ion adsorption; and recovery of phosphate ions (using sodium hydroxide solution) were evaluated. BE granulated by PET (BE-PET30S) could be successfully used for phosphate-ion removal by adsorption. The specific surface area and amount of hydroxyl groups of BE-PET30S were found to be 119.8 m²/g and 1.4 mmol/g, respectively. Granulated BEs reached equilibrium adsorption capacities within 24 h. The phosphate-ion-adsorption rate data were fitted to the pseudo-second-order kinetic model (r²=0.981–0.998). The adsorption isotherm data were fitted to both the Freundlich (0.987–0.989) and Langmuir (0.905–0.944) equations. Based on the thermodynamic study, it was found that the phosphate-ion adsorption by granulated BEs is a spontaneous and exothermic process. The phosphate ions adsorbed onto BE-PET30S could be easily recovered by using a sodium hydroxide solution (1–1000 mmol/L) and their recovery percentage was found to be between 63.3% and 94.0%. The results obtained from this study could be useful for recovering phosphate ions and preventing problems related to water pollution.

Key words phosphate; adsorption; boehmite; polyethylene terephthalate

Phosphates from industrial, agricultural, and domestic wastewater are the major sources of excessive phosphate pollution in water bodies. Phosphate is the key limiting nutrient for biological and chemical processes in natural water bodies. However, large quantity of phosphate in aquatic environment is one of the main causes of eutrophication in surface water bodies. Therefore, it is necessary to develop an efficient method for removing excess phosphate in order to prevent water pollution. Various methods have been developed for phosphate removal, including chemical precipitation, biological treatment, ion exchange and ion adsorption. Adsorption is one of the most attractive approaches for phosphate removal because of its practical advantages such as operation simplicity, low operation cost, and effective removal of the adsorbed substances without generating any harmful by-products. Different types of adsorbent materials have been used, such as red mud, fly ash, calcined dolomite, and Fe–Mn binary oxides.

Large amounts of bauxite (aluminum ore) are used to produce aluminum. Bauxite mainly consists of gibbsite and boehmite (BE). BE is an inexpensive, easily processed, and recyclable raw material. Its molecular formula is AlO(OH)₃; it is colorless and insoluble in water, acid or base residence, thermal residence. Granulated BE—with or without a binder—was prepared for phosphate removal. However, many of the available binders (or a regular mixture of binders) could not be used for granulating BE because of the need for a solvent to solubilize them. Polyethylene terephthalate (PET), a thermoplastic resin, is insoluble in water and resistant to heat. PET easily melts when heated and stiffens upon cooling. Therefore, PET (binder) would easily granulate BE (adsorbent). Moreover, PET binder is superior to others (ethyl cellulose and vinyl acetate etc.) with respect to environmental safety and cost-effectiveness. However, the phosphate-ion-adsorption capacity of BE (granulated with PET) has not been reported yet.

In this study, we synthesized granulated BEs using PET, and their properties such as adsorption capacity, effects of contact time, temperature, and solution pH on phosphate-ion adsorption were investigated. Finally, the recovery of phosphate ions adsorbed onto the granulated BE surface using a sodium hydroxide solution was evaluated.

Experimental

Materials BE (aluminum oxyhydroxide) was purchased from Tomita Pharmaceutical Co., Ltd., Japan. The main chemical composition of BE is Al(OH)₃ and contains <0.1% Cl⁻ and <0.8% SO₄²⁻ ions. The mass loss of BE upon drying, its pH, mean particle size, and pore volume were 7.8%, 8.2, 100 µm, and 0.402 mL/g, respectively. Granular BEs were prepared by mixing PET (20 v/v, 25 v/v, 30 v/v, and 35 v/v%) with BE, and the mixtures (e.g., BE-PET20, BE-PET25, BE-PET30, and BE-PET35) were heated on a hotplate. Next, the mixture was dried at 100°C for 24 h. The particle diameters of granular BE (BE-PET) thus prepared were 500–840 µm (S), 840–1680 µm (M), and 1680–2000 µm (L), where S, M, and L stand for small, medium, and large sizes, respectively.

Scanning electron microscopy (SEM) was performed using a JSM-5200 (JEOL, Japan). X-Ray diffraction (XRD) was obtained by a MiniFlex II (Rigaku, Japan). The specific surface area, mean pore diameter, and pore volume of the granular BE samples were measured by using a NOVA4200e specific surface analyzer (Yuasa Ionic, Japan). The number of hydroxyl groups was measured by fluoride-ion adsorption, and the pH of solutions was measured using a digital pH (Mettler-Toledo) after adding the adsorbent (BE-PET, 1 g) to 50 mL distilled water, kept still for 2 min at 25°C, and filtrated through a 0.45-

* To whom correspondence should be addressed. e-mail: kawasaki@phar.kindai.ac.jp © 2013 The Pharmaceutical Society of Japan
μm membrane filter.

**Amount of Adsorbed Phosphate Ions at Saturation**

Granular BE (BE-PET30, 0.05 g) was added to a 50 mL solution of phosphate ions (500 mg/L). The resulting suspension was shaken at 25°C for 24 h at 100 rpm, and then filtered through a 0.45-μm membrane filter. The concentration of phosphate ions was measured using DR/890 colorimeter (Hach, U.S.A.). The amount of desorbed phosphate ions was calculated by using Eq. 2:

\[
D = \frac{C_d V}{M}
\]

where \(D\) is the amount of the desorbed phosphate ions (mg/g), \(C_d\) is the concentration of phosphate ions after desorption (mg/L), \(V\) is the volume of solvent (L), and \(M\) is the mass of the adsorbent (g).

**Effect of Contact Time on the Adsorption of Phosphate Ions onto BE-PET30S**

Granular BE (BE-PET30S, 0.05 g) was added to a 50 mL solution of phosphate ions (50 mg/L). The resulting suspension was shaken at 25°C for 0.5–48 h at 100 rpm. The amount of the adsorbed phosphate ions onto BE-PET30S was calculated from the difference in the concentration before and after adsorption as follows (Eq. 1):

\[
X = \frac{(C_0 - C_e)V}{M}
\]

where \(X\) is the amount of phosphate ion adsorbed (mg/g), \(C_0\) is the concentration before adsorption (mg/L), \(C_e\) is the concentration after adsorption (mg/L), \(V\) is the volume of solvent (L), and \(M\) is the mass of the adsorbent (g).

**Effect of Solution pH on the Adsorption of Phosphate Ions onto BE-PET30S**

Granular BE (BE-PET30S, 0.05 g) was added to a 50 mL solution of phosphate ions (50 mg/L), and the pH of the solution was adjusted using either a hydrochloric acid or sodium hydroxide solution. The resulting suspensions were shaken at 25°C for 24 h at 100 rpm. The amount of phosphate ions adsorbed onto BE-PET30S is calculated by using Eq. 1.

**Adsorption Isotherms of Phosphate Ions onto BE-PET30S**

Granular BE (BE-PET30S, 0.05 g) was added to a 50 mL solution of phosphate ions (50 mg/L), and the pH of the solution was adjusted using either a hydrochloric acid or sodium hydroxide solution. The resulting suspensions were shaken at 25°C for 24 h at 100 rpm. The amount of phosphate ions adsorbed onto BE-PET30S is calculated by using Eq. 1.

**Recovery Percentage of Phosphate Ions from BE-PET30S Using a Sodium Hydroxide Solution**

BE-PET30S (0.05 g) was added to a 50 mL solution of phosphate ions (50 mg/L). The resulting suspension was shaken at 25°C for 24 h at 100 rpm. The amount of phosphate ions adsorbed onto BE-PET30S was calculated by using Eq. 1.

### Table 1. Properties of BE and BE-PET

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m²/g)</th>
<th>Mean pore diameter (Å)</th>
<th>Pore volume (mL/g)</th>
<th>Amount of hydroxyl group (mmol/L)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Micropore (r ≤ 10 Å)</td>
<td>Mesopore (10 &lt; r ≤ 250 Å)</td>
<td>Macropore (250 Å &lt; r)</td>
</tr>
<tr>
<td>BE</td>
<td>310.0</td>
<td>23.0</td>
<td>&lt;0.001</td>
<td>0.355</td>
<td>0.001</td>
</tr>
<tr>
<td>PET</td>
<td>2.1</td>
<td>12.0</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>BE-PET20L</td>
<td>88.9</td>
<td>36.6</td>
<td>0.002</td>
<td>0.161</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>BE-PET20M</td>
<td>102.1</td>
<td>36.3</td>
<td>0.002</td>
<td>0.183</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>BE-PET20S</td>
<td>125.7</td>
<td>35.9</td>
<td>0.002</td>
<td>0.223</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>BE-PET25L</td>
<td>89.2</td>
<td>33.7</td>
<td>0.003</td>
<td>0.147</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>BE-PET25M</td>
<td>91.3</td>
<td>33.9</td>
<td>0.002</td>
<td>0.152</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>BE-PET25S</td>
<td>130.6</td>
<td>33.8</td>
<td>0.002</td>
<td>0.218</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>BE-PET30L</td>
<td>81.2</td>
<td>33.6</td>
<td>0.002</td>
<td>0.134</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>BE-PET30M</td>
<td>87.6</td>
<td>34.1</td>
<td>0.002</td>
<td>0.147</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>BE-PET30S</td>
<td>119.8</td>
<td>33.9</td>
<td>0.002</td>
<td>0.200</td>
<td>0.001</td>
</tr>
<tr>
<td>BE-PET35L</td>
<td>57.1</td>
<td>32.8</td>
<td>0.002</td>
<td>0.091</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>BE-PET35M</td>
<td>67.7</td>
<td>32.6</td>
<td>0.002</td>
<td>0.107</td>
<td>0.001</td>
</tr>
<tr>
<td>BE-PET35S</td>
<td>91.2</td>
<td>33.4</td>
<td>0.002</td>
<td>0.149</td>
<td>0.001</td>
</tr>
</tbody>
</table>

The data are presented as mean of 3 experiments.

### Results and Discussion

**Properties of BE and BE-PET**

Table 1 shows the physicochemical properties of BE and BE-PET. The specific surface area and amount of hydroxyl groups of BE are 310.0 m²/g and 1.5 mmol/g and the corresponding values for PET are 2.1 m²/g and 0.2 mmol/g, respectively. The specific surface area of BE-PET (S) is greater than that of BE-PET (M or L). The pore volumes and mesopores of BE-PET also showed similar trends. However, the amount of hydroxyl groups did not change (1.1–1.5 mmol/g) among BE-PET(S), (M), and (L). The pH of the aqueous solutions of BE, PET, and BE-PET were 7.8, 7.1, and 6.6–7.0, respectively.

**Amount of Phosphate Ions at Saturation**

The amount of
phosphate ions adsorbed onto BE-PET at saturation is shown in Fig. 1. The results show that the amount of the phosphate ions adsorbed onto BE-PET followed the order: L < M < S. These results proved that BE-PET exhibited similar trends in specific surface areas and mesopores. Therefore, the adsorption of phosphate ions onto BE-PET may be related to their specific surface area and mesopore properties. Previous studies reported that the adsorption mechanism of phosphate ions onto BE involved the ion-exchange phenomena with the hydroxyl groups on the BE surface.8,9 However, in this study, the adsorption mechanism of phosphate ions (onto BE-PET) is different because BE was granulated with PET resulting in the masking of the BE surfaces (by PET). Furthermore, the amount of phosphate ions adsorbed onto BE-PET30 was greater than that onto BE-PET20, BE-PET25, and BE-PET35. Therefore, the optimal content of binder (PET) for phosphate-ion adsorption is 30%. For this reason, we selected BE-PET30 for subsequent adsorption experiments. The amount of phosphate ions adsorbed onto BE-PET30S (41.7 mg/g) was greater than that onto other adsorbents. The phosphate ions adsorption maximum onto calcined dolomite, iron hydroxide-egg shell, Fe–Mn binary oxides, activated carbon, and wood aspen fibers are 48.4, 14.49, 22.99, 29.44, and 4.3 mg/g, respectively.4–6 These results suggested that granulated BEs (BE-PET30) could be very useful for phosphate-ion adsorption.

**XRD and SEM Images of BE-PET30** The XRD and SEM images of BE and BE-PET are shown in Figs. 2 and 3, respectively. BE structural features were found to be maintained by the granulated BEs: BE-PET20, BE-PET25, and BE-PET30. However, the BE structure was found to be destroyed...
at BE-PET35, which indicated that BE might have been completely masked by binder PET35. Figure 3 shows that BEs could be granulated with PET binders, and both BE and BE-PET30(S) have the same particle diameter. Therefore, granular BEs could be obtained with PET binders.

**Effect of Contact Time on Phosphate-Ion Adsorption onto BE-PET30**

Figure 4 shows the adsorption rate of phosphate ions onto BE-PET30, which reached equilibrium within 24 h. The amount of phosphate ions adsorbed followed the order: BE-PET30 (L)<BE-PET30 (M)<BE-PET30 (S), which suggested that the adsorption of phosphate ions might be related with specific surface area and mesopore volume. The adsorption kinetics were further evaluated by using the pseudo-first-order and pseudo-second-order kinetic models.

The pseudo-first-order kinetic model can be expressed as follows:11) (Eq. 3):

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

The pseudo-second-order kinetic model can be expressed as follows:12) (Eq. 4):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where \(q_e\) is the equilibrium adsorption amount (mg/g), \(q_t\) is the adsorption amount (mg/g) at time \(t\) (h), and \(k_1\) and \(k_2\) are the pseudo-first-order and pseudo-second-order rate constants (g/mg h), respectively. Table 2 lists the fitting parameters of phosphate-ion adsorption to BE-PET30 using the pseudo-first-order and pseudo-second-order kinetic models. The values of \(r>0.981\) indicated that the pseudo-second-order kinetic model best describes the measured data and thus supports the assumption behind the model that the adsorption is due to chemisorption.12,13) In addition, the values of equilibrium adsorption calculated from the fitting results are nearly identical to the experimental data, further confirming that the kinetics of phosphate-ion adsorption to BE-PET30 follows a pseudo-second-order reaction rate.14)

**Adsorption Isotherms of Phosphate Ions onto BE-PET30S**

The adsorption isotherms of phosphate ions onto BE-PET30S at different temperatures are shown in Fig. 5. The amount of adsorbed phosphate ions increased with increasing temperature. The experimental data were applied to the Langmuir and Freundlich isotherm equations. The Langmuir equation was applied to the adsorption equilibrium of phosphate ions onto BE-PET30S as follows:15) (Eq. 5):

$$\frac{C_e}{q_e} = \frac{1}{W_s a} + \frac{C_e}{W_s}$$

where \(C_e\) is the equilibrium concentration (mg/L), \(q_e\) is the amount of phosphate ions adsorbed to BE-PET30S at equilibrium (mg/g), and \(W_s\) and \(a\) are Langmuir constants related to monolayer adsorption capacity and energy of adsorption, respectively.

The Freundlich equation is represented by the following expression:15) (Eq. 6):

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

<table>
<thead>
<tr>
<th>Samples</th>
<th>(q_{e,exp})</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k_1 (h^{-1}))</td>
<td>(q_{e,calc} (mg/g))</td>
<td>(r)</td>
</tr>
<tr>
<td>BE-PET30L</td>
<td>9.14</td>
<td>0.07</td>
<td>7.9</td>
</tr>
<tr>
<td>BE-PET30M</td>
<td>9.84</td>
<td>0.08</td>
<td>7.8</td>
</tr>
<tr>
<td>BE-PET30S</td>
<td>14.65</td>
<td>0.11</td>
<td>9.9</td>
</tr>
</tbody>
</table>

Fig. 4. Adsorption Rate of Phosphate Ion onto BE-PET30

Initial concentration of phosphate: 50 mg/L, Sample volume: 50 mL, Adsorbent: 0.05 g, Temperature: 25°C, Contact time: 0.5–48 h, 100 rpm. The data are presented as mean of 3 experiments.

Fig. 5. Adsorption Isotherms of Phosphate Ion onto BE-PET30S at Different Temperatures

Initial concentration of phosphate: 5–100 mg/L, Sample volume: 50 mL, Adsorbent: 0.05 g, Temperature: 25°C, Contact time: 24 h, 100 rpm. The data are presented as mean of 3 experiments.
where $k$ (mg/g) is the Freundlich capacity constant and $n$ is the Freundlich intensity constant. The fitted constants for the Langmuir and Freundlich isotherm models along with correlation coefficients are summarized in Table 3. As shown in Table 3, higher correlation coefficients indicate that the Freundlich model (0.987–0.989) fits the adsorption data much better than the Langmuir model (0.905–0.944). When $1/n$ falls in the range 0.1–0.5, the adsorbate is considered to be easily adsorbed. In contrast, if $1/n > 2$, adsorption is considered to be difficult. In this study, $1/n$ is found to be between 0.2 and 0.3; therefore, phosphate ions were easily adsorbed onto BE-PET30S.

Moreover, taking account of using BE-PET30S in the fields, the concentration of phosphate ion in the effluent from industry is thought to be below 8 mg/L. Amount of phosphate ion adsorbed onto BE-PET30S (Initial concentration: 5–10 mg/L) was 3.2–8.3 mg/g in this study. These results suggested that BE-PET30S would be found to be useful for the adsorption of phosphate ion in the fields.

**Thermodynamic Study** The thermodynamic parameters of the phosphate-ion-adsorption process are determined with the experimental data (Fig. 5) by using the following equations\(^{16}\) (Eqs. 7, 8):

\[
\ln K_c = \Delta S / R - \Delta H / RT \quad (7)
\]

\[
\Delta G = \Delta H - T \Delta S \quad (8)
\]

where $\Delta S$, $\Delta H$, and $\Delta G$ are the changes in standard entropy, enthalpy, and Gibbs free energy, respectively; $R$ (8.314 J/mol K) is the gas constant; $T$ (K) is the absolute temperature; and $K_c$ (mg/L) is the equilibrium stability constant defined by $q_e / C_e$. By plotting a graph of $\ln K_c$ versus $1/T$, the values of $\Delta H$ and $\Delta S$ can be estimated from the slopes and intercepts, respectively. Table 4 shows that phosphate-ion adsorption is a spontaneous and an exothermic process (from $\Delta G$ and $\Delta H$ values\(^{17}\)). The positive value of $\Delta S$ suggests an increased randomness at the solid/solution interface that facilitates phosphate-ion adsorption onto BE-PET30S.

**Effect of Solution pH on Phosphate-Ion Adsorption onto BE-PET30S** The amount of phosphate ions adsorbed onto BE-PET30S at different pH conditions is shown in Fig. 6. Phosphate-ion adsorption onto BE-PET30S was highly pH dependent. As pH increases from 2.0 onward, the amount of phosphate-ion adsorption also increases. The maximum value of phosphate-ion adsorption was achieved at pH 4.0. A further increase in pH decreased the adsorption. The observed trend in adsorption is related to phosphate-proton-dissociation equilibrium. Different phosphate species dominate at different pH values, as shown by the following equations:

\[
\begin{align*}
\text{H}_3\text{PO}_4 & \leftrightarrow \text{H}_2\text{PO}_4^- + \text{H}^+ (K_1) \\
\text{H}_2\text{PO}_4^- & \leftrightarrow \text{HPO}_3^{2-} + \text{H}^+ (K_2) \\
\text{HPO}_3^{2-} & \leftrightarrow \text{PO}_4^{3-} + \text{H}^+ (K_3)
\end{align*}
\]

Table 3. Freundlich and Langmuir Constants of Adsorption Isotherms of Phosphate Ion onto BE-PET30S

<table>
<thead>
<tr>
<th>Samples</th>
<th>Freundlich constants</th>
<th>Langmuir constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5°C</td>
<td>25°C</td>
</tr>
<tr>
<td></td>
<td>$1/n$</td>
<td>$r$</td>
</tr>
<tr>
<td>BE-PET30S</td>
<td>0.3</td>
<td>0.989</td>
</tr>
</tbody>
</table>

Table 4. Thermodynamic Parameters for Adsorption of Phosphate Ion onto BE-PET30S

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol K)</th>
<th>$\Delta G$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>−39.0</td>
<td>2.14</td>
<td>−635.3</td>
</tr>
<tr>
<td>10</td>
<td>−34.5</td>
<td>1.75</td>
<td>−521.7</td>
</tr>
<tr>
<td>20</td>
<td>−13.2</td>
<td>0.61</td>
<td>−183.3</td>
</tr>
<tr>
<td>30</td>
<td>−14.4</td>
<td>0.63</td>
<td>−189.1</td>
</tr>
<tr>
<td>50</td>
<td>−13.3</td>
<td>0.52</td>
<td>−158.4</td>
</tr>
<tr>
<td>75</td>
<td>−12.8</td>
<td>0.45</td>
<td>−137.6</td>
</tr>
<tr>
<td>100</td>
<td>−13.9</td>
<td>0.47</td>
<td>−145.5</td>
</tr>
</tbody>
</table>

Fig. 6. Amount of Phosphate Ion Adsorbed onto BE-PET30S at Different pH Conditions

Initial concentration of phosphate: 50 mg/L, Sample volume: 50 mL, Adsorbent: 0.05 g, Temperature: 25°C, Contact time: 24 h, 100 rpm. The data are presented as mean of 3 experiments.
where $pK_1=2.13$, $pK_2=7.20$, and $pK_3=12.33$.

At pH $<2.13$, the predominant phosphate species is H$_3$PO$_4$, which is weakly attached to the adsorbent sites. When pH is in the range 2.13–7.20, BE-PET30S performed well in the presence of dominant monovalent H$_3$PO$_4$ species. Therefore, in this study, the chief mechanism of phosphate-ion adsorption involves ion exchange between the phosphate and hydroxyl groups on the BE-PET30S surface.

**Recovery Percentage of Phosphate Ions from BE-PET30S Using a Sodium Hydroxide Solution** The desorption percentage of phosphate ions from BE-PET30S is shown in Fig. 7. The figure shows that when 1 mmol/L sodium hydroxide solution was used, the desorption percentage was 63.3%, which increased with increasing concentration of sodium hydroxide solution; the desorption percentages using 1, 10, 100, and 1000 mmol/L sodium hydroxide solution were 63.3%, 72.7%, 91.0%, and 94.0%, respectively. Phosphate ions might be desorbed as sodium phosphate (e.g., NaH$_2$PO$_4$, Na$_2$HPO$_4$, and Na$_3$PO$_4$). However, we could not confirm it. If phosphate ions are desorbed as sodium phosphate, it can be used as food additives, fertilizer, pharmaceuticals, etc.

Moreover, amount of phosphate adsorbed onto or desorbed from BE-PET30S is shown in Fig. 8. The amount of phosphate adsorbed for first, second, and third time was 38.0 mg, 26.8 mg, and 5.4 mg, respectively; the amount of desorbed was 21.3%, 10.2%, and 35.6%, respectively. These results suggest that regeneration of the surface hydroxyl groups on BE-PET30S using a sodium hydroxide solution was possible, and successive ion exchange with surface hydroxyl groups on BE-PET30S occurred three times.

**Conclusion**

BE had been successfully granulated by PET to form granulated BE (BE-PET) that was used to evaluate phosphate-ion-removal capacity by adsorption process. The optimum content of PET binder to effectively granulate BE was found to be 30%. The amount of phosphate ions adsorbed onto BE-PET surface followed the order: BE-PET30 (L)<BE-PET30 (M)<BE-PET30 (S). BE-PETs reached equilibrium adsorption capacities within 24 h. The phosphate-ion-adsorption rate data followed a pseudo-second-order kinetic model rather than a pseudo-first-order kinetic model. The amount of phosphate ions adsorbed onto BE-PET30S obviously increased with increasing temperature. The phosphate-ion adsorption isotherm data were fitted to both the Freundlich and Langmuir equations, which suggested that a monolayer adsorption had occurred. Furthermore, the results of thermodynamic study prove that the phosphate-ion adsorption is a spontaneous and an exothermic process. The positive values of ΔS suggest that the increased randomness at the solid/solution interface facilitates phosphate-ion removal from BE-PET30S surface. The optimal range of pH for phosphate-ion adsorption was found to be 2.0–4.0. The phosphate ions adsorbed using BE-PET30S could be easily recovered by sodium hydroxide solution as sodium phosphate.

**Acknowledgment** This research was supported partly by MEXT KAKENHI Grant Number 24710083.