Adsorption of phosphate ions from an aqueous solution by calcined nickel-cobalt binary hydroxide

Fumihiko Ogata, Erimi Ueta, Megumu Toda, Masashi Otani and Naohito Kawasaki

ABSTRACT

Different molar ratios of a Ni/Co binary hydroxide (NiCo82, NiCo91, and Ni100) were prepared and calcined at 270 °C (NiCo82-270, NiCo91-270, and Ni100-270). The properties of the adsorbents and the amount of adsorbed phosphate ions were evaluated. The adsorbents calcined at 270 °C had a nickel oxide structure. The amount of adsorbed phosphate ions, the amount of hydroxyl groups, and the specific surface area of the calcined adsorbents at 270 °C were greater than those of the uncalcined adsorbents. The amount of adsorbed phosphate ions was related to the amount of hydroxyl groups and the specific surface area; the correlation coefficients were 0.966 and 0.953, respectively. The adsorption isotherm data for NiCo91 and NiCo91-270 were fit to both the Freundlich and Langmuir equations. The amount of adsorbed phosphate ions increased with increasing temperature. The experimental data fit the pseudo-second-order model better than the pseudo-first-order model. A neutral pH was optimal for phosphate ion adsorption. In addition, the phosphate ions that were adsorbed onto NiCo91-270 could be recovered using sodium hydroxide, and the adsorbent was useful for the repetitive adsorption/desorption of phosphate ions. Collectively, these results suggest that NiCo91-270 is prospectively useful for the adsorption of phosphate ions from aqueous solutions.

INTRODUCTION

Phosphates are essential and often limiting nutrients in most aquatic environments and can accelerate eutrophication, leading to an increase of the cost of water treatment (Dodds et al. 2008), a decrease of the recreational value of the waterway (Daniel et al. 1998), and the formation of harmful algal blooms that may pose a risk to human health from the production of cyanotoxins (Anderson et al. 2002). In fact, the presence of trace amounts of phosphate (even less than 1 mg/L) in municipal and industrial treated wastewater is often responsible for eutrophication in receiving water bodies (Zhao & Sengupta 1998). Therefore, removing phosphate is a necessity before discharging wastewater into water bodies (Zhang et al. 2009).

Various approaches have been developed for the removal of phosphate from water, including chemical precipitation, adsorption, biological removal, reverse osmosis, membrane technologies, ion exchange, and constructed wetlands (Choi et al. 2012; Zhang et al. 2012; Jeong et al. 2014; Qiu et al. 2014; Sowmya & Meenakshi 2014; Yoshino et al. 2014). Among these available approaches, chemical precipitation and biological processes are generally not able to meet the stringent effluent standards, while ion exchange and membrane technologies need high investments and have a high operation cost. Compared to these methods, adsorption processes have the advantages of an easily handled operation, high efficiency, and lower cost (Liu et al. 2012).

Mixed metal (hydr)oxides exhibit surface properties that mimic natural systems more closely than their individual components. Multi-component sorbents demonstrate physicochemical properties significantly different from those of their single-component counter parts. It is the differences in the physicochemical properties that are considered the major reasons for differences in sorption behavior between the multi- and single-component systems (Harvey & Rhue 2002). For example, the increased fixation of Cu and Pb in
the Fe/Al oxide system (compared to their single-component counter parts) is attributed to an increased surface area and surface charge (Potter & Yong 1999; Dong et al. 2000). In addition, Al-Fe hydr(oxide), Fe-Mn binary oxide, Fe-Zr binary oxide, and Fe-Al-Mn trimetal oxide have been reported for phosphate ion adsorption (Harvey & Rhue 2008; Zhang et al. 2009; Long et al. 2011; Lü et al. 2015).

Recently, we demonstrated the adsorption capability of phosphate ions by nickel hydroxide or cobalt hydroxide in a calcination treatment (single-component material) (Ogata et al. 2015, 2016). These materials showed an efficient adsorption capacity of phosphate ions from aqueous solutions. Therefore, we anticipate that a nickel-cobalt binary hydr(oxide) originating from the combination of nickel hydroxide and cobalt hydroxide will have the potential for phosphate removal. However, no information is available for phosphate adsorption by nickel-cobalt binary hydroxide with different nickel/cobalt molar ratios (from 8:2 to 10:0) (Zhang et al. 2009).

The object of this study was to explore the feasibility of the nickel and cobalt binary hydr(oxide) for phosphate removal. We examined the surface characteristics of the adsorbent. The kinetic and isothermal behaviors of phosphate ion adsorption were investigated. The parameters influencing phosphate ion removal were also studied, including the solution pH and temperature. Additionally, phosphate ion desorption from the adsorbent was performed to assess the regeneration feasibility.

MATERIAL AND METHODS

Materials

NiCo82 (molar ration of Ni/Co is 8:2), NiCo91 (molar ration of Ni/Co is 9:1), and Ni100 (molar ration of Ni/Co is 10:0) as coprecipitation hydroxides were purchased from Kansai Catalyst Co., Ltd (Japan). The adsorbent was placed in a muffle furnace, and the desired temperature (270 °C) was maintained for 2 h to obtain NiCo82-270, NiCo91-270, and Ni100-270, respectively (Ogata et al. 2014). The specific surface area of the adsorbent was measured using a NOVA4200e specific surface analyzer (Yuasa Ionic, Japan). The morphologies and crystallinities of the adsorbent were studied using scanning electron microscopy (SEM, SU1510, Hitachi, Ltd, Japan) and X-ray diffractometry (XRD, MiniFlex II, Rigaku, Japan). Thermo-gravimetry-differential thermal analysis (TG-DTA) was performed using a TG8120 thermogravimetric analyzer (Shimadzu, Japan). The amount of hydroxyl groups was measured using the fluoride ion adsorption method (Yamashita et al. 1978). The solution pH was measured by a digital pH meter (Metttler-Toledo, Japan) after adding the adsorbent (0.1 g) to distilled water at pH 7.0 (50 mL), allowing the mixture to stand for 2 min at 25 °C, and filtering it through a 0.45 μm membrane filter. The distribution of phosphorous on the adsorbent was measured using an electron microanalyzer (EPMA, JXA-8530F, JEOL, Japan) at an accelerating voltage of 15.0 kV and a beam diameter of 10 μm.

Amount of adsorbed phosphate ions

The adsorbent (0.1 g) was added to a solution (50 mL) containing phosphate ions (initial concentration of 500 mg/L). The suspension was shaken at 100 rpm for 24 h at 25 °C. The sample was then filtered through a 0.45 μm membrane filter, and the filtrate was analyzed using adsorption spectrophotometry (DR/890, HACH, USA). The concentration of the phosphate ions was determined using the ascorbic acid reduction method (Kofinas & Kioussis 2003). The amount of phosphate ions adsorbed onto the adsorbent was calculated using Equation (1):

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

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

Amount of adsorbed phosphate ions at different conditions

First, the adsorbent (NiCo91 and NiCo91-270, 0.1 g) was added to the phosphate ion solution (50 mL, 100 mg/L). The sample solution was shaken at 25 °C for 1 min, 10 min, 1 h, 5 h, 8 h, 16 h, 20 h, 24 h, and 32 h at 100 rpm. Then, the adsorbent (NiCo91 and NiCo91-270, 0.1 g) was added to the phosphate ion solution (50 mL, 20–100 mg/L). The sample solution was shaken at 1, 25, and 50 °C for 24 h at 100 rpm. Finally, the adsorbent (NiCo91 and NiCo91-270, 0.1 g) was added to the phosphate ion solution at different pH conditions (50 mL, 100 mg/L, and pH 1–12). The pH in the solution was adjusted using sodium hydroxide and hydrochloric acid. The sample solution was shaken at 25 °C for 24 h at 100 rpm. The adsorbed amount was calculated using Equation (1).
Phosphate adsorption and desorption capability

The adsorbent (NiCo91-270, 0.6 g) was added to the phosphate ion solution (300 mL, 250 mg/L). The sample solution was shaken at 25 °C for 24 h at 100 rpm. Subsequently, the suspension was filtered through a 0.45 μm membrane filter, and the sample solution was measured using the adsorption spectrophotometer. The amount of adsorbed phosphate ions was calculated using Equation (1).

After adsorption, the adsorbent was collected, dried, and then used for the desorption experiment. The collected adsorbent was added to a 50 mL solution of 1, 10, 100, and 1,000 mmol/L sodium hydroxide. The suspension was shaken at 100 rpm for 24 h at 25 °C. Then, the suspension was filtered through a 0.45 μm membrane filter. The concentration of phosphate ions was measured using the adsorption spectrophotometer. The amount desorbed was calculated using Equation (2).

\[
d = \frac{C_e V}{W}
\]  

(2)

where \(d\) is the amount of desorbed phosphate ions (mg/g), \(C_e\) is the concentration after the desorption (mg/L), \(V\) is the solvent volume (L), and \(W\) is the weight of the adsorbent sample (g).

RESULTS AND DISCUSSION

Properties of the adsorbents

SEM images of the adsorbents are shown in Figure 1. All samples consisted of spherical particles of various diameters. We observed that the calcination treatment hardly affected the adsorbent surfaces. XRD patterns of the adsorbents are shown in Figure 2. The obtained data were consistent with powder diffraction file 2010 obtained from the International Center for Diffraction Data. Accordingly, the uncalcined adsorbents (NiCo82, NiCo91, and Ni100) mainly consisted of nickel hydroxide, while the adsorbents calcined at 270 °C (NiCo82-270, NiCo91-270, and Ni100-270) consisted of nickel oxide. Previous studies of heating nickel hydroxide metals have proposed two types of chemical reactions (Mani & Neufville 1988; Natarajan et al. 1997; Ogata et al. 2014): (i) dehydration, which corresponds to the loss of the adsorbed and/or structurally bonded water below 250 °C and (ii) decomposition of nickel hydroxide to nickel oxide, when nickel hydroxide is heated at temperatures >250 °C. In addition, the crystal structure of cobalt hydroxide was maintained below 130 °C but destroyed above 140 °C. Further, cobalt oxide was formed at 150 °C (Yang et al. 2010; Ogata et al. 2016). In this study, similar trends were observed, and thus, it was
clear that the crystalline nature of the adsorbents was unaffected by adding cobalt.

The results for the thermal analysis of the adsorbents are shown in Figure 3. An endothermic peak at approximately 270 °C on the DTA curve of the uncalcined adsorbent was observed; the TG curve showed a sharp 20 wt% weight loss. This corresponds to the decomposition of nickel hydroxide to nickel oxide and water. Two or three peaks were detected on the DTA curves of the calcined adsorbent at 270 °C. The DTA curves of all samples (NiCo82-270, NiCo91-270, and Ni100-270) showed a slight weight loss, which corresponds to the loss of adsorbed water at approximately 100 °C. In addition, a previous study reported that mass loss step in cobalt hydroxide attributed to the reaction $6\text{Co(OH)}_2 + \text{O}_2 \rightarrow 2\text{Co}_3\text{O}_4 + 6\text{H}_2\text{O}$, $2\text{Co}_3\text{O}_4 \rightarrow 6\text{CoO} + \text{O}_2$ (approximately 300–900 °C). The data obtained in this study (NiCo82-270 and NiCo91-270) are similar to that of a previous study (Yang et al, 2010). Finally, the endothermic peak at 277 °C (Ni100-270) may show that uncalcined Ni100 (the residues) was calcined and changed from nickel hydroxide to nickel oxide in this experimental condition.

These findings suggest that calcination in the range 250–270 °C can promote the conversion of nickel hydroxide to nickel oxide, and that cobalt hardly affects the structure of the nickel hydroxides.

The amount of hydroxyl groups, specific surface area, and surface pH for each adsorbent are shown in Table 1. The amount of hydroxyl groups and the specific surface area of the calcined adsorbents at 270 °C (amount of hydroxyl groups: 1.3–1.5 mmol/g, specific surface area: 125.1–142.6 m$^2$/g) were greater than those of the uncalcined
adsorbents (amount of hydroxyl groups: 0.6–0.8 mmol/g, specific surface area: 11.6–18.6 m²/g). The calcination treatment would be useful for increasing the amount of hydroxyl groups and the specific surface area (improving the properties of the adsorbents). Our previous report showed that the specific surface area of nickel hydroxide increased suddenly at 260°C, which indicated that the presence of the nickel oxide species affected the increasing specific surface area of the adsorbent (Ogata et al. 2014). The addition of cobalt hardly affected the amount of hydroxyl groups and the specific surface area. In addition, the surface pH did not change drastically from the calcination treatment.

**Amount of adsorbed phosphate ions**

The amount of phosphate ion adsorbed on the adsorbent is shown in Figure 4. The calcination treatment increased the amount of adsorbed phosphate ions. Furthermore, after phosphate ion adsorption, the amount of phosphate ions increased, suggesting that the phosphate ion adsorption was related to the nature of the adsorbent surface (Figure 5). Therefore, we investigated the relationship between the amount of adsorbed phosphate ions and the amount of hydroxyl groups or the specific surface area associated with the adsorbent (Figure 6). These results indicate that the amount of adsorbed phosphate ions was related to the amount of hydroxyl groups and the specific surface area. The observed relationship suggests that the phosphate ions were exchanged with the surface hydroxyl groups on the adsorbent.

**Effect of contact time on phosphate ion adsorption**

The effect of the contact time on the adsorption of phosphate ions is shown in Figure 7. The phosphate ion adsorption reached equilibrium within 16 h. The experimental data (Figure 7) were analyzed using different models to evaluate the mechanism of adsorption and the potential rate controlling steps, such as the mass transport and diffusion control processes. Initially, the pseudo-first-order and the pseudo-second-order models were tested to describe the adsorption process. The mathematical representations of these models are given in Equations (3) and (4), respectively (Ren et al. 2012):

\[
\ln \left( \frac{q_e}{q_t} \right) = \ln q_e - k_1 t 
\]

\[
t = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} 
\]

where \(q_e\) and \(q_t\) are the amounts of phosphate ions adsorbed at equilibrium and at time \(t\) (mg/g), respectively, \(k_1\) is the rate constant of the pseudo-first-order model adsorption (1/h), and \(k_2\) is the rate constant of the pseudo-second-order model adsorption (g/mg/h). A plot of \(t/q_t\) versus \(t\) should provide a linear relationship if pseudo-second-order kinetics is applicable, and a plot of \(\ln (q_e - q_t)\) versus \(t\) should be linear if pseudo-first-order kinetics is applicable (Lalley et al. 2016).

The calculated regression coefficients for the kinetic models are documented in Table 2. The regression coefficients of the pseudo-second-order model (>0.989 for all adsorbents) were the best for representing phosphate ion adsorption, while the pseudo-first-order model regression coefficients were below 0.983, indicating this model was not applicable. In addition, the value of \(q_{e,\text{exp}}\) for NiCo91
and NiCo91-270 was much closer to the value of $q_{e,cal}$ and the pseudo-second-order model than that of the pseudo-first-order model. The success of the pseudo-second-order model in fitting the experimental data suggests that the mechanism of adsorption is determined by chemisorption (Ho & McKay 1998; Lalley et al. 2016; Ogata et al. 2016).

Effect of pH on phosphate ion adsorption

Figure 8 shows the effect of pH on the adsorption of phosphate ions by NiCo91 and NiCo91-270. The data clearly demonstrate that the adsorption was pH dependent. The adsorption capacity was high at neutral pH, and the adsorption capacity decreased when the solution pH was increased to basic pH conditions. Similar phenomena were observed by other researchers in studies of phosphate ion adsorption by binary metal oxides (Zhang et al. 2009; Liu et al. 2012; Li et al. 2014; Ogata et al. 2015; Su et al. 2015; Tofik et al. 2016). Phosphate ion adsorption would become more favorable at a neutral pH than at a high pH. Phosphate exists as H$_2$PO$_4^-$, HPO$_4^{2-}$, and PO$_4^{3-}$ depending on the pH of the solution, with $pK_{a1} = 2.15$, $pK_{a2} = 7.20$, and $pK_{a3} = 12.33$, respectively. It can be assumed that H$_2$PO$_4^-$ ions are the predominant species in the pH range of 3–6, while HPO$_4^{2-}$ ions appear to be the more dominant species at higher pH values. Reports indicate that the H$_2$PO$_4^-$ species are more easily adsorbed on the metal (hydr)oxide surfaces than other species (Rodrigues & da Silva 2009; Lai et al. 2016). In acidic conditions (<pH 2), phosphate exists as H$_3$PO$_4$, which is not the anion (ion form). Therefore, the adsorbed amount was very low. In contrast, H$_2$PO$_4^-$ and HPO$_4^{2-}$ were the dominant phosphate species in the solution in
the pH range of 3–10. A lower pH was favorable for the protonation of the adsorbent surface. The increased protonation was thought to increase the positively charged sites, enlarge the attraction force existing between the sorbent surface and the phosphate anions and, therefore, increase the amount of adsorption in the lower pH region (Zhang et al. 2009). In alkaline conditions, the negatively charged sites on the surface of the adsorbent became dominant, and the amount of negatively charged phosphate species increased, which resulted in the repulsion between the phosphate ions and the adsorbent. In addition, decreasing for phosphate ion adsorption capacity should be attributed to the competition between the hydroxyl ions and the phosphate ions on the adsorbent surface (Liu et al. 2008; Li et al. 2014).

### Adsorption isotherms of phosphate ion

Adsorption isotherms of phosphate ions at different temperatures are shown in Figure 9. The amount of phosphate ions adsorbed onto NiCo91 and NiCo91-270 increased with increasing temperature (the amount of phosphate ions adsorbed onto NiCo91-270 at 25 and 50 °C showed a similar trend for NiCo91-270). The adsorption data for 50 °C shows a process with two adsorption layers (it is quite clear for NiCo91-270 from 20 mg/L and for NiCo91 from 40 mg/L). Further studies are needed to elucidate the adsorption mechanism in detail. In addition, it is important to clarify the details of the mechanism of phosphate ion adsorption onto adsorbents in future work. Langmuir and Freundlich models were used to describe the phosphate ion adsorption capacity of NiCo91 and NiCo91-270 (Chubar et al. 2005; Li et al. 2006; Biswas et al. 2008; Lin et al. 2013). The Langmuir model was appropriate for monolayer adsorption onto the surface of the adsorbent. All the adsorption sites were equal and the number of identical sites limited the adsorption capacity. The equation for the Langmuir model is shown below:

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

The Freundlich model is often applicable to describe the models of multilayer adsorption onto the surface of

<table>
<thead>
<tr>
<th>Samples</th>
<th>(q_e,\text{exp (mg/g)})</th>
<th>(k_1 (\text{h}^{-1}))</th>
<th>(q_e,\text{cal (mg/g)})</th>
<th>(r)</th>
<th>(k_2 (\text{g/mg/h}))</th>
<th>(q_e,\text{cal (mg/g)})</th>
<th>(r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCo91</td>
<td>7.0</td>
<td>0.002</td>
<td>2.4</td>
<td>0.844</td>
<td>5.9</td>
<td>6.8</td>
<td>0.989</td>
</tr>
<tr>
<td>NiCo91-270</td>
<td>22.1</td>
<td>0.002</td>
<td>3.9</td>
<td>0.983</td>
<td>995.6</td>
<td>21.7</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Figure 7 | Effect of contact time on the adsorption of phosphate ion.

Figure 8 | Amount of adsorbed phosphate ion at different pH condition.
heterogeneous sites with different bond energies. The equation for the Freundlich model is given as follows:

$$\log q_e = \log k + \left( \frac{1}{n} \right) \log C_e$$  \hspace{1cm} (6)

where $q_e$ and $W_S$ are the amount and maximum amount of adsorbed phosphate per unit weight of adsorbent (mg/g), respectively, $C_e$ is the residual concentration of the adsorbate in the bulk solution (mg/L), $a$ is a constant determined by plotting $C_e/q_e$ versus $C_e$, $\log k$ and $1/n$ are the constants related to the adsorption of the adsorbent and the intensity of the adsorption, respectively (Ogata et al. 2016).

The calculated parameters are summarized in Table 3. The correlation coefficients indicate that both the Freundlich (0.953–0.991) and Langmuir (0.900–0.995) isotherm equations provided good fits for the phosphate ion adsorption data on NiCo91 and NiCo91-270. Moreover, the value of the Langmuir constant ($W_S$) increased with increasing temperature, in agreement with the observation of phosphate ion adsorption in the isotherms (Figure 9). The value of $W_S$ for NiCo91-270 was greater than that for NiCo91, which indicated that NiCo91-270 possessed a good phosphate ion adsorption capability. In addition, phosphate ions were easily adsorbed onto the adsorbent surface when $1/n$ was in the range 0.1–0.5, but not when $1/n > 2$. This finding is also consistent with previous reports, according to which phosphate ion adsorption on the adsorbent surface readily occurred when $1/n < 2$ (0.17–0.56) (Abe et al. 1976). The Freundlich constant ($\log k$) parameters of the Freundlich equation ranged from −0.14 to 0.74 for NiCo91 and 0.89 to 1.03 for NiCo91-270. These values reveal the lower affinity of NiCo91 towards phosphate ions than NiCo91-270.

### Thermodynamic parameters

The determination of the thermodynamic state functions ($\Delta G$, $\Delta H$, and $\Delta S$) is useful to understand the nature of adsorption. These can be estimated from the Langmuir
isotherm data with the following relationships (Hameed et al. 2011):

\[
\Delta G = -RT \ln K \quad (7)
\]

\[
\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (8)
\]

where \( R \) (8.134 J/mol K) is the gas constant, \( T \) (K) is the absolute temperature, and \( K \) is the standard thermodynamic equilibrium constant defined by \( q_e/C_e \). By plotting the graph of \( \ln K \) versus \( 1/T \), the values of \( \Delta H \) and \( \Delta S \) can be estimated from the slopes and intercept (Liu & Zhang 2015).

The thermodynamic parameters for the adsorption of phosphate ions are shown in Table 4. The \( \Delta G \) value decreased when the temperature was increased from 274 to 318 K, suggesting an increase in the reaction spontaneity (from 3.28 to \(-0.05\) kJ/mol and from \(-4.10\) to \(-6.42\) kJ/mol for NiCo91 and NiCo91-270, respectively). The decrease of the \( \Delta G \) value with increasing temperature revealed that the adsorption of phosphate ions onto the adsorbent became more favorable at higher temperatures. This fact was previously confirmed by the isotherm experiments at different temperatures. The positive \( \Delta S \) values reflect the affinity of the phosphate ions for the adsorbent and also show the increased randomness at the solid-solution interface. Moreover, the positive \( \Delta H \) value confirmed the endothermic nature of the adsorption process, which was also demonstrated by the enhancement of the phosphate ion adsorption at higher temperatures (Tu et al. 2012; Ogata et al. 2015).

### Adsorption or desorption of phosphate ions

The regeneration of the used NiCo91-270 using sodium hydroxide solution and re-adsorption were investigated to assess its reusability. These adsorption-regeneration cycles were performed up to three times, and the results are shown in Figure 10. The experiment demonstrated that

![Figure 10](https://iwaponline.com/wst/article-pdf/75/1/94/456847/wst075010094.pdf)

**Figure 10** | Recovery of phosphate ion from NiCo91-270 using sodium hydroxide.

<table>
<thead>
<tr>
<th>Samples</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></td>
<td></td>
<td>274 K</td>
</tr>
<tr>
<td>NiCo91</td>
<td>21.8</td>
<td>1.0</td>
<td>3.28</td>
</tr>
<tr>
<td>NiCo91-270</td>
<td>9.2</td>
<td>47.4</td>
<td>-4.10</td>
</tr>
</tbody>
</table>

Table 4 | Thermodynamic parameters for the adsorption of phosphate ions
NiCo91-270 could be recovered with a sodium hydroxide solution at a certain concentration, and that the recovered NiCo91-270 could be recycled. The total amount of phosphate adsorbed and desorbed, and the recovery percentage were, respectively, 55.3 mg/g, 40.0 mg/g, and 66.9% with 1 mmol/L, 77.2 mg/g, 50.4 mg/g, and 65.3% with 10 mmol/L, 82.7 mg/g, 60.9 mg/g, and 73.7% with 100 mmol/L, and 86.2 mg/g, 77.9 mg/g, and 90.4% with 1,000 mmol/L sodium hydroxide. The amount of desorbed phosphate ions increased compared to the amount adsorbed at cycle 3 for the 100 and 1,000 mmol/L sodium hydroxide solutions, which indicates that the adsorbed phosphate ions at cycle 1 and 2 were released from the adsorbent. However, in general, the observations from the desorption experiment still prove that NiCo91-270 could be recovered and reused for phosphate ion adsorption using a sodium hydroxide solution as the eluent. In other words, NiCo91-270 has the potential for application as a renewable adsorbent (Liu et al. 2012; Yang et al. 2015; Ogata et al. 2015).

Comparison of adsorption capacities

Table 5 summarizes the reported adsorption capacities of various adsorbents on phosphate (Zeng et al. 2004; Namasi-vayam & Prathap 2005; Rodrigues & da Silva 2010; Ogata et al. 2012; Lü et al. 2013; Ogata et al. 2015), compared to NiCo91 and NiCo91-270. The phosphate ion adsorption capacity of NiCo91-270 was the highest among these reported adsorbents (except for the Fe-Mn binary oxide).

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Mn binary oxide</td>
<td>36.0</td>
<td>17</td>
</tr>
<tr>
<td>Magnetic Fe-Zr binary oxide</td>
<td>15.6</td>
<td>18</td>
</tr>
<tr>
<td>Fe-Zr oxide</td>
<td>15.7</td>
<td>18</td>
</tr>
<tr>
<td>Iron oxide tailings</td>
<td>8.2</td>
<td>44</td>
</tr>
<tr>
<td>Hydrous Nb oxide</td>
<td>15.0</td>
<td>45</td>
</tr>
<tr>
<td>Fe-Cr oxide</td>
<td>6.5</td>
<td>46</td>
</tr>
<tr>
<td>Granular boehmite</td>
<td>8.4</td>
<td>47</td>
</tr>
<tr>
<td>NiCo82</td>
<td>5.8</td>
<td>This study</td>
</tr>
<tr>
<td>NiCo91</td>
<td>7.5</td>
<td>This study</td>
</tr>
<tr>
<td>Ni100</td>
<td>5.0</td>
<td>This study</td>
</tr>
<tr>
<td>NiCo82-270</td>
<td>22.2</td>
<td>This study</td>
</tr>
<tr>
<td>NiCo91-270</td>
<td>22.3</td>
<td>This study</td>
</tr>
<tr>
<td>NiCo100-270</td>
<td>18.2</td>
<td>This study</td>
</tr>
</tbody>
</table>

From such comparisons, NiCo91-270 is expected to be employed in a commercial process in the future for the adsorption and recovery of phosphate ions from contaminated aqueous solutions.

CONCLUSIONS

Three types of adsorbents (NiCo82, NiCo91, and Ni100) were tested to adsorb phosphate ions from aqueous solution. The adsorbents calcined at 270 °C (NiCo82-270, NiCo91-270, and Ni100-270) were prepared in this study. The uncalkined and calcined adsorbents had nickel hydroxide and nickel oxide structures, respectively. The amount of hydroxyl groups and the specific surface area of the calcined adsorbent were greater than those of the uncalkined adsorbent. Moreover, the addition of cobalt hardly affected the properties of the adsorbents. The amount of phosphate ions adsorbed onto NiCo91-270 was higher than the other adsorbents. The amount of adsorbed phosphate ions was related to both the amount of hydroxyl groups ($R^2 = 0.966$) and the specific surface area ($R^2 = 0.953$). The adsorption equilibrium for NiCo91-270 was reached within 16 h, and these data were subsequently fitted to a pseudo-second-order model ($R^2 = 0.999$). A neutral pH was optimal for phosphate ion adsorption. The amount of phosphate ions adsorbed increased, and value of $\Delta G$ decreased with increasing temperature in the 274–318 K range. This decrease in $\Delta G$ value with temperature revealed that phosphate ion adsorption onto the adsorbent became more favorable at higher temperatures. The adsorption isotherm data provided a good fit to both the Freundlich and Langmuir equations. The adsorbed phosphate ions could be desorbed by washing with sodium hydroxide (1, 10, 100, and 1,000 mmol/L). In addition, the adsorption/desorption cycles could be repeated at least three times, indicating that NiCo91-270 had a great potential as a renewable adsorbent. Taken together, the results obtained in this study illustrate that the novel NiCo91-270 has promising applications for phosphate ion adsorption from aqueous solutions.

ACKNOWLEDGEMENTS

MEXT (Ministry of Education, Culture, Sports, Science and Technology)-supported Program for the Strategic Research Foundation at Private Universities, 2014-2018 (S1411037).


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