Phosphate recovery from an aqueous solution through adsorption-desorption cycle
over thermally treated activated carbon

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In the present study, we tested nine commercially available activated carbons for their abilities to recover phosphate ion from an aqueous solution by a temperature swing method, in which phosphate ion was adsorbed at 303 K, followed by desorption and recovery in pure water at 373 K. While the activated carbon made from coconut shell and manufactured by Nakarai Tesque Inc. (trade name: Charcoal Activated) had a moderate adsorption capacity at 303 K, little amount of phosphate ion was adsorbed on it at 373 K, meaning that it was an appropriate adsorbent for the temperature swing method. Since the adsorbed amounts of phosphate ion for various activated carbons at 303 K were correlated with the number of basic sites on them and were significantly increased as pH of the solution decreased, it is presumed that phosphate ion was adsorbed on the basic sites of the activated carbons with electrostatic interaction mediated by protons. High-temperature thermal treatment of the activated carbon in a vacuum increased the recovered amount of phosphate ion. This increase was brought about by elimination of oxygen-containing functional groups from the activated carbon. By using activated carbon obtained by the thermal treatment at 1273 K for 3 h, 86% of phosphate ion was recovered from an aqueous solution with 1.0 mmol L\(^{-1}\) of phosphate ion through the temperature swing between 303 and 373 K. The
thermally treated activated carbon was reusable at least three times without any severe performance loss.

Keywords:
Phosphate recovery; adsorption; activated carbon; temperature swing; thermal treatment
1. Introduction

Soil tends to be deficient in phosphorus, which is a nutrient essential for plant growth [1,2]. Thus, fertilization of the soil with phosphorus-containing fertilizer is necessary to effectively grow the crops that support the world’s growing population. In addition to the use in fertilizer, the scope of utilization of phosphorus compounds is being extended to various products, including food additives, detergents, pesticides, metal coatings, fire retardants, medicines, and paints [3,4]. In short, phosphorus is an indispensable element of modern society and will continue to be in the future.

Most of the phosphorus compounds used in fertilizer and other chemicals are produced commercially from phosphate rock. However, since phosphate rock is a non-renewable resource and the demand for it is expected to undergo rapid growth, future depletion of the phosphorus supply is a concern [5-7]. In addition to the issue of resource depletion, phosphate causes eutrophication in lakes, ponds, and bays, if domestic sewage, municipal wastewater, and agricultural runoff are discharged into the environment without appropriate treatment [8]. Thus, a system to effectively recover phosphate ion from effluent is urgently needed for sustainable phosphorus procurement and aquatic conservation [6,9-12].
While the recovery of phosphate ion by crystallization of magnesium ammonium phosphate hexahydrate and hydroxyapatite in wastewater has been studied extensively [13-20], recently, adsorption over adsorbents for the recovery of phosphate ion has also been investigated intensively especially for water containing low concentration phosphate ion [21-27]. Various adsorbents and anion exchangers including granular ferric hydroxide [28], lanthanum hydroxide [29], magnetite/lanthanum hydroxide hybrid [30], zirconium-containing solid materials [31-34], double-layered hydroxides [35-38] were found to show high adsorption capacity for phosphate ion. However, a large volume of regeneration solution is necessary to decompose the formed metal phosphates for the crystallization method or to strip phosphate ion off adsorbents to recover it, and these are major disadvantages of these methods.

As a method for recovery of phosphate ion with adsorbents, an adsorption-desorption cycle by temperature swing, in which adsorption and desorption of phosphate ion are performed at different temperatures, has been proposed. Ideally, this method, which is called a temperature swing method here, does not need any regenerating solution, while heating the adsorbent is necessary to provoke the desorption of phosphate ion. Thus, the temperature swing method is potentially environmentally benign for the recovery of phosphate ion. Gotoh et al. developed a
thermosensitive gel adsorbent and applied it to the recovery of phosphate ion by the temperature
swing method [39]. The gel adsorbent synthesized by copolymerization of N-isopropylacrylamide
with N-[3-(dimethylamino)propyl]acrylamide has a specific volume phase transition temperature,
below which its hydrophobicity-hydrophilicity changes drastically. Below the volume phase transition
temperature, the gel swells in water due to its hydrophilic nature, and thus phosphate ion is
incorporated into the gel. After the incorporation of phosphate ion, the temperature of the gel is
increased above the volume phase transition temperature for it to release phosphate ion. However,
handling of the gel adsorbent is too difficult for practical application, especially with a
commercial-scale plant, because changes in the volume of the gel adsorbent through the
adsorption-desorption cycle are too large, owing to the volume phase transition, making the
operation difficult. In addition, the gel adsorbent is too soft to be used in conventional
commercial-scale plants.

Since adsorption over a common solid surface is often exothermic with a decrease in entropy,
Gibbs free energy of adsorption is increased as the temperature increases [40]. Thus, it is possible
that the adsorption capacity of an adsorbent is decreased as the temperature increases. Accordingly,
we hypothesized that phosphate ion could be recovered from solutions by the temperature swing
method even over conventional adsorbents. Activated carbons (ACs) are commonly used adsorbents for water and air purifications, adsorption-separation processes, decoloration, and so on [41-44]. Removal of phosphate ion from the solution by the adsorption on activated carbons and related compounds has been investigated [45-48], but desorption (elution) of phosphate ion from them have not been intensively concerned so far. In the present study, we applied commercial ACs to the recovery of phosphate ion from an aqueous solution by the temperature swing method. In addition, thermal treatment of AC was investigated to increase its adsorption capacity for phosphate ion. An adsorption model for phosphate ion on AC was discussed based on the adsorption isotherms and dependence of the adsorbed amount on the pH of the solution.

2. Experimental

2.1. Activated carbon samples and thermal treatment

Commercial AC samples used in this study are listed in Table 1 along with surface area and ash content. Granular AC was crushed in a mortar to obtain a powdered sample. Prior to use, AC was pretreated in boiling water to remove water-soluble impurities as follows. Powdery AC (3 g) was added to distilled water (50 mL), and the suspension was heated with vigorous stirring at
reflux temperature for 24 h. After cooling down to room temperature, the AC was recovered by filtration, washed with distilled water several times, and then dried at 373 K overnight.

AC-Naca-CocoShe (Table 1), which was the most effective adsorbent for the recovery of phosphate ion as described in detail in the results and discussion, was thermally treated under vacuum. Powdery AC-Naca-CocoShe (2 g) was placed on a quartz boat in a quartz tube. The inside of the quartz tube was evacuated, and the sample was heated at 403 K for 1 h to remove physisorbed water. Then, the temperature was further increased to 1273 K at a rate of 10 K min\(^{-1}\) and kept for 3 h under vacuum. After cooling down to room temperature under vacuum, the sample was taken out from the tube. To investigate the influences of temperature and time on thermal treatment, AC-Naca-CocoShe was treated at 1073–1373 K and for 1–12 h. The thermally treated samples are denoted as AC-xK-yh, where \(x\) and \(y\) indicate the temperature and duration of the treatment, respectively (Table 2).

2.2. Characterization

The surface area of AC was estimated by applying the Brunauer–Emmett–Teller (BET) equation to an adsorption isotherm of N\(_2\) measured at 77 K, which was acquired on a Belsorp-
mini instrument (BEL Japan Inc.). Before the measurement, AC was pretreated in a stream of \( \text{N}_2 \) at 473 K for 3 h. To determine ash content, AC was heated in air at 1123 K for 3 h to clear off combustible matter. In this study, the residual matter after the combustion was regarded as ash. The carbon content of AC was analyzed by using an elemental analyzer (ECS 4010; Costech Instruments).

The numbers of acid and basic sites on AC were quantified by Boehm titration [49-51]. Powderly AC (0.12 g) was added to 15 mL of aqueous NaOH solution (0.1 mol L\(^{-1}\)). The suspension was stirred at 303 K for 24 h, during which acidic sites on AC were neutralized with NaOH. After 24 h, the AC was separated by filtration, and the resulting filtrate was titrated with dilute hydrochloric acid (0.05 mol L\(^{-1}\)) to determine the number of acidic sites on AC. To determine the number of basic sites, AC was treated in hydrochloric acid (0.1 mol L\(^{-1}\)) at 303 K for 24 h and removed from the suspension by filtration. An aqueous solution of NaOH (0.1 mol L\(^{-1}\)) was added to the filtrate, and the mixture was titrated with dilute hydrochloric acid (0.05 mol L\(^{-1}\)).

The pH of the aqueous suspension in which powdery AC was dispersed was measured to evaluate the acidity or basicity on the AC surface. The aqueous suspension (10 mL) containing
0.1 g of AC was stirred for 10 min, and the pH of the suspension was measured by using a pH 

meter (Metrohm, Model 827 pH lab).

A temperature-programmed desorption (TPD) profile for AC-Naca-CocoShe was measured 

by using a Multitask TPD system equipped with a mass spectrometer. After the sample was 

pretreated in a flow of He at 403 K for 1 h, the temperature of the sample was raised to 1273 K at 

a rate of 10 K min\(^{-1}\) with monitoring the signals of \(m/e = 18, 28,\) and 44, which correspond to 

\(\text{H}_2\text{O}, \text{CO},\) and \(\text{CO}_2,\) respectively.

2.3. Adsorption experiment for phosphate ion over activated carbons

An aqueous solution of KH\(_2\text{PO}_4\) (Wako Pure Chem. Ind. Ltd., 1.0 mmol L\(^{-1}\), pH 5.1) was used 

for the adsorption experiments. As the abundance ratio of phosphate ions under equilibrium 

conditions calculated from the equilibrium constants shows (Fig. S1 in Supporting Information), 

\(\text{H}_2\text{PO}_4^-\) was the predominant species in the solution with pH 5.1. The solution (10 mL) and AC 

(0.1 g) were added to a test tube, and the resulting suspension was vigorously stirred at 303 K. A 

small portion was withdrawn from the suspension at 24 h, followed by centrifugation to separate 

AC. The concentration of phosphate ion in the supernatant was determined by using an ion
chromatograph (Tosoh Co. Ltd., IC-2001) with a column (TSK gel Super IC-AZ, Tosoh) and an electrical conductivity detector. A mixed aqueous solution of NaHCO$_3$ (2.9 mmol L$^{-1}$) and Na$_2$CO$_3$ (3.1 mmol L$^{-1}$) was used as eluting solution. The adsorbed amount of phosphate ion on AC at a certain time was calculated according to eq. 1:

$$Q = \frac{C_0 - C_t}{M} V$$  \hspace{1cm} (1)$$

where $C_0$ (= 1.0 mmol L$^{-1}$) and $C_t$ [mmol L$^{-1}$] are the initial concentration and concentration of phosphate ion at time $t$, respectively, $V$ [L] is the volume of the solution, and $M$ [g] is the weight of AC. After 24 h, the temperature was raised to 373 K and a small portion of the suspension was quickly withdrawn by using a syringe with a separation filter.

An adsorption isotherm of phosphate ion on AC was measured at 303 K by changing the initial concentration of KH$_2$PO$_4$ over a range of 0.5 to 20 mmol L$^{-1}$, while the adsorption time was fixed at 24 h. In addition, effect of dose of AC on the adsorption of phosphate ion was investigated at 303 K by changing the amount of AC added to an aqueous solution of KH$_2$PO$_4$ (1.0 mmol L$^{-1}$, 10 mL) over a range of 0.1 to 1.0 g, while the adsorption time was fixed at 24 h.

2.4. Recovery of phosphate ion through temperature swing with activated carbon
First, AC (5.0 g) was added to an aqueous solution of KH$_2$PO$_4$ (50 mL, 1.0 mmol L$^{-1}$), and the suspension was stirred vigorously at 303 K. After 5 h, AC was taken out from the suspension by filtration, and the concentration of phosphate ion in the filtrate was measured. The AC was dried in an oven at 333 K overnight.

Next, desorption of phosphate ion from the AC, on which phosphate ion was adsorbed in advance, was performed in fresh distilled water at 373 K as follows. The AC was added to 25 mL of distilled water, and the suspension was heated with vigorous stirring at 373 K. A small portion of the suspension was periodically withdrawn and analyzed by ion chromatography. After 4 h, the AC was separated from the suspension by filtration, keeping the suspension hot to avoid re-adsorption of phosphate ion on the AC. The resulting AC was dried in air at 333 K overnight and then reused for the recovery of phosphate ion.

3. Results and discussion

3.1. Adsorption and recovery of phosphate ion over activated carbon

Fig. 1 shows the adsorbed amounts of phosphate ion over various ACs at 303 and 373 K for 24 h, which are denoted as $Q_{303K}$ and $Q_{373K}$, respectively. The amounts calculated by subtracting
Q_{373K} from Q_{303K}, which is denoted as M_{\text{diff}}, are also shown in Fig. 1. M_{\text{diff}} corresponds to the amount of potentially recoverable phosphate ion by the temperature swing between 303 and 373 K. When M_{\text{diff}} is negative, it is given as zero in Fig. 1. Adsorption properties were substantially different depending on the ACs. Except for AC-Naca-Sawd and AC-MCEvo-PetroRe, M_{\text{diff}} was positive, indicating that recovery of phosphate ion from the solution was possible by the temperature swing. While AC-Naca-Coal had the largest Q_{303K}, which was 0.057 mmol g\(^{-1}\) (= 5.4 mg g\(^{-1}\) as PO\(_4^{3-}\)), Q_{373K} was also the largest among the AC samples. Thus, M_{\text{diff}} of AC-Naca-Coal was moderate. In contrast, Q_{303K} was not so large for AC-Naca-CocoShe, but Q_{373K} was negligible, resulting in the largest M_{\text{diff}} (= 0.029 mmol g\(^{-1}\) = 2.8 mg g\(^{-1}\) as PO\(_4^{3-}\)) among the ACs. Thus, we further investigated AC-Naca-CocoShe for the recovery of phosphate ion.

Because adsorption is a phenomenon occurring on a solid surface, it is expected that adsorbed amounts of phosphate ion are correlated with surface areas of ACs. However, there was no clear correlation between adsorption capacity and surface area (Fig. S2 in Supporting Information). Another factor that is likely to affect the adsorption capacity is ash content, because the ash in AC is commonly sodium and calcium oxides or hydroxide, which can form phosphorus salts by reacting with phosphate ion. However, no correlation between the adsorption capacities
and ash content was observed (Fig. S3 in Supporting Information). Therefore, it was suggested that acidic and basic sites on ACs were involved in the adsorption of phosphate ion over ACs. This will be discussed in detail later.

Next, we investigated the amount of AC-Naca-CocoShe necessary for complete removal of phosphate ion from the solution with 1.0 mmol L\(^{-1}\) of phosphate ion. As Fig. S4 in Supporting Information shows, the concentration of phosphate ion after the adsorption for 24 h was decreased with increase in the dose of AC-Naca-CocoShe and almost all phosphate ion was removed when the dose was 100 g L\(^{-1}\) (= 1.0 g/10 mL). Thus, we applied this dose for the recovery of phosphate ion through the temperature swing.

Fig. 2 shows the results for the recovery of phosphate ion through the temperature swing between 303 and 373 K over AC-Naca-CocoShe. First, phosphate ion was adsorbed on AC-Naca-CocoShe at 303 K (Fig. 2(A)). In a separate experiment, we confirmed that the adsorption of phosphate ion reached near equilibrium at 5 h and thus we decided that the time for adsorption was 5 h. At the time, 97\% of phosphate ion was removed from the solution, at which AC-Naca-CocoShe adsorbed 0.0097 mmol g\(^{-1}\) (=0.92 mg g\(^{-1}\) as PO\(_4^{3-}\)) of phosphate ion. Then, AC-Naca-CocoShe was separated from the suspension by filtration and dried (Fig. 2(B)). The resulting AC-
Naca-CocoShe was added to fresh distilled water and the temperature of the suspension was kept at 373 K. It takes note that the fresh distilled water used for the desorption of phosphate ion was half the volume of the aqueous solution for the adsorption in order to concentrate phosphate ion for the recovery. The concentration of phosphate ion in the water was increased and reached to 1.46 mmol L$^{-1}$ at 4 h. With the temperature swing between 303 and 373 K, 73% of phosphate ion was successfully recovered.

We further investigated the reusability of AC-Naca-CocoShe for the recovery of phosphate ion (Fig. 3). As already shown, 0.0097 mmol g$^{-1}$ (=0.92 mg g$^{-1}$ as PO$_4^{3-}$) of phosphate ion was adsorbed on AC-Naca-CocoShe at 303 K, and 73% of it was desorbed at 373 K for the first use. For the first reuse, however, the adsorbed amount was decreased to 0.0065 mmol g$^{-1}$ (=0.62 mg g$^{-1}$ as PO$_4^{3-}$), and only 85% of it was desorbed at 373 K. The adsorbed amount was further decreased to 0.0052 mmol g$^{-1}$ (=0.49 mg g$^{-1}$ as PO$_4^{3-}$), and desorbed amount of phosphate ion at 373 K was only 0.0050 mmol g$^{-1}$ (=0.48 mg g$^{-1}$ as PO$_4^{3-}$) for the second reuse, which corresponds to only 71% of the amount of phosphate ion recovered in the first use. This means that AC-Naca-CocoShe had a problem for reuse. Since the surface area and total pore volume of AC-Naca-CocoShe after the second reuse were almost the same as those of the fresh one (1281 m$^2$ g$^{-1}$ →...
1293 m² g⁻¹ and 0.54 cm³ g⁻¹ \rightarrow 0.55 cm³ g⁻¹), the decrease in the performance for the recovery
of phosphate ion might be caused by irreversible adsorption of phosphate ion. Improvement in
the reusability of AC-Naca-CocoShe was achieved by thermal treatment, which will be described
later.

3.2. Thermal treatment of AC-Naca-CocoShe in vacuum

Generally, ACs have various functional groups on the surface, and the type and amount have
great impacts on their adsorption properties [52-55]. We thus investigated thermal treatment of
AC-Naca-CocoShe to increase the recoverable amount of phosphate ion (M_{diff}) and to improve
the reusability. Fig. 4 shows influence of the temperature in the thermal treatment for AC-Naca-
CocoShe on Q_{303K}, Q_{373K}, and M_{diff}. Thermal treatment increased Q_{303K}. Treatment at 1273 K or
higher was especially effective at increasing Q_{303K}. Q_{303K} for the sample treated at 1373 K (AC-
1373K-3h) was approximately double that of the parent AC-Naca-CocoShe. While Q_{373K} was also
increased by thermal treatment, the increase in Q_{303K} was more pronounced. As a result, M_{diff} was
enhanced by the thermal treatment. AC-1373K-3h had an M_{diff} of 0.048 mmol g⁻¹ (= 4.6 mg g⁻¹
as PO₄³⁻), which was approximately 1.7 times larger than that of the parent AC-Naca-CocoShe
(0.028 mmol g$^{-1}$ = 2.7 mg g$^{-1}$ as PO$_4^{3-}$).

Next, optimization of the duration of the thermal treatment was investigated using AC-Naca-CocoShe, while the temperature was fixed at 1273 K. The results are shown in Fig. 5. $Q_{303K}$, $Q_{373K}$, and $M_{\text{diff}}$ were increased as the treatment time was extended, but the degree of the increment slowed down for 3 h or longer. The sample obtained by treatment at 1273 K for 12 h, AC-1273K-12h, had an $M_{\text{diff}}$ of 0.039 mmol g$^{-1}$ (= 3.75 mg g$^{-1}$ as PO$_4^{3-}$).

To determine the effect of the thermal treatment on the adsorption property for phosphate ion in detail, adsorption isotherms of phosphate ion at 303 K were measured on AC-Naca-CocoShe and AC-1273K-3h (Fig. 6). For both AC samples, the adsorbed amounts of phosphate ion were increased sharply at low concentrations and then approached a constant, giving a Langmuir-type adsorption isotherm. This type of isotherm meant that phosphate ion was strongly adsorbed on the samples and that a homogeneous monolayer was formed. The isotherms were analyzed with the Langmuir adsorption equation (eq. 2):

$$Q_e = \frac{Q_{\text{max}}KC}{1+KC}$$  \hspace{1cm} (2)

where $C$, $Q_e$, $Q_{\text{max}}$, and $K$ are the equilibrium concentration (mmol L$^{-1}$), amount of adsorbed phosphate ion at $C$ (mmol g$^{-1}$), maximum adsorbed amount of phosphate ion (mmol g$^{-1}$), and
adsorption coefficient (L mmol⁻¹), respectively. It was found that \( Q_{\text{max}} \) for AC-1273K-3h (0.14 mmol g⁻¹ = 13 mg g⁻¹ as PO₄³⁻) was about three times larger than that for AC-Naca-CocoShe (0.045 mmol g⁻¹ = 4.3 mg g⁻¹ as PO₄³⁻). On the other hand, the adsorption coefficient for AC-1273K-3h (1.1 L mmol⁻¹) was smaller than that for AC-Naca-CocoShe (3.9 L mmol⁻¹). The decrease in the adsorption coefficient suggests that most adsorption sites formed by the thermal treatment were different to those originally present on AC-Naca-CocoShe and had a weak affinity for phosphate ion.

3.3. Adsorption model for phosphate ion on activated carbon

Normally, ACs have a graphite structure, consisting of graphene sheets in a stacked arrangement. It is known that oxygen-containing functional groups, including carboxyl, lactone, ether, phenolic hydroxyl, acid anhydride, and quinone groups, are present at the edges and carbon vacancies in graphene sheets. Most of the oxygen-containing functional groups can be eliminated by thermal treatment in a vacuum or inert atmosphere with the formation of CO, CO₂, and H₂O [56]. For AC-Naca-CocoShe, the formations of CO and CO₂ were observed on the temperature-programmed desorption (TPD) profile (Fig. S5), while H₂O formation was not pronounced over
the whole temperature range. In addition to the oxygen-containing functional groups, the graphene sheet has delocalized π electrons that show basicity [57-59]. It is supposed that the acid and base functions greatly influence the adsorption properties of ACs for phosphate ion in water. Thus, we measured the numbers of acidic and basic sites on AC-Naca-CocoShe and samples obtained by its thermal treatment.

Table 2 summarizes the numbers of acidic and basic sites on AC-Naca-CocoShe and samples obtained by thermal treatment under different conditions. In addition, the surface areas and pH of the aqueous suspension in which the AC samples were dispersed are also given in Table 2. The numbers of acidic and basic sites on AC-Naca-CocoShe were 0.33 and 0.31 mmol g⁻¹, respectively. It is known that when the AC is in water, acidic (A-H) and basic (B_π) sites on AC react with water according to eqs. 3 and 4.

\[ \text{A-H} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+ \]  
\[ \text{B_π} + \text{H}_2\text{O} \rightleftharpoons \text{B_π-H}^+ + \text{OH}^- \]  

Since the pH of the aqueous suspension of AC-Naca-CocoShe was 8.45, in spite of the number of acidic sites being slightly larger than that of the basic ones, the reaction described by eq. 4 was dominant over the one described by eq. 3, indicating that the basic sites were stronger than the
298 acidic ones.

299 The number of acidic sites decreased and that of basic ones increased as the temperature and
time for the thermal treatment was increased (Table 2), while the change in surface area was small.

301 There were few acidic sites on AC-1373K-3h (0.08 mmol g⁻¹) but many basic ones (0.74 mmol
302 g⁻¹); the latter was more than double the number of basic sites on AC-Naca-CocoShe. In addition,
the pH of the aqueous suspension with the AC sample was increased as the temperature and time
for the thermal treatment was increased. The trend in pH was consistent with the changes in the
numbers of acidic and basic sites with the thermal treatment. The carbon content involved in AC-
Naca-CocoShe was 91.2% and increased up to 98.0% and 99.6% for AC-1273K-3h and AC-
1373K-3h, respectively. The increase in the carbon content clearly indicated the elimination of
oxygen-containing functional groups. Through elimination, the carbonization of AC progressed
and consequently, more basic sites corresponding to delocalized \( \pi \) electrons were formed,
especially at near edges of graphene sheets.

311 In Fig. 7, the amounts of adsorbed phosphate ion are plotted as a function of the number of
basic sites on AC-Naca-CocoShe and the samples obtained by the thermal treatment under
different conditions. The result shows that the amount of adsorbed phosphate ion was positively
correlated with the number of basic sites, suggesting that the basic sites on the AC samples were
deeply involved in the adsorption of phosphate ion. As mentioned above, protons formed by
reaction with water are present over the basic sites of AC (eq. 4), on which the protons presumably
interact with delocalized π electrons. Consequently, the surface of the AC was positively charged
in water if the basic sites are predominant, as in the AC samples obtained by thermal treatment.
On the other hand, phosphate ion was present mainly as HPO$_4^{2-}$ in solution at pH of
approximately 8 (Fig. S1 in Supporting Information). Based on this, we propose models for the
adsorption of phosphate ion on the AC samples as shown in Fig. 8. Basically, phosphate ion
(HPO$_4^{2-}$) may interact electrostatically with H$^+$ over the basic site on the surface (Fig. 8(a)). In
addition to such interactions, phosphate ion may interact with oxygen-containing functional
groups at the edge of and defects in the graphene sheet through hydrogen bonding (Fig. 8(b)) if
they exist, like in AC-Naca-CocoShe, resulting in the strong adsorption of phosphate ion. We
presume that phosphate ion interacting with oxygen-containing functional groups may make a
covalent bond such as an ester (Fig. 8(b)), forming irreversibly adsorbed phosphate species that
never desorb, even at 373 K. That may cause a deterioration in the reusability of the untreated
AC-Naca-CocoShe (Fig. 3).
As Fig. 7 shows, the number of adsorbed phosphate ion in the AC samples at 303 K under the present conditions was only about one tenth of the number of basic sites. All the AC samples used in this study gave a type I adsorption isotherm for N\textsubscript{2} at 77 K (Fig. S6 in Supporting Information), indicating that they were microporous materials. The size of micropores estimated from the $t$-plot, which was calculated from the corresponding N\textsubscript{2} adsorption isotherms, were about 0.8 nm for all the samples (Fig. S6 in Supporting Information). On the other hand, the molecular size of the phosphate ion estimated on the basis of its structure is approximately 0.6 nm. Thus, it is possible for phosphate ion to enter micropores. In fact, a significantly large amount of phosphate ion was adsorbed on Ac-Naca-CocoShe and AC-1273K-3h when the adsorption experiment was carried out under low pH conditions (Fig. S7 in Supporting Information), while pH under standard conditions was around 8, supporting the speculation mentioned above. As we propose in Fig. 8, phosphate ion is adsorbed on basic sites of AC via electrostatic interactions between phosphate ion and H\textsuperscript{+} on AC. Since the amount of H\textsuperscript{+} on AC was not so large under the standard conditions due to the mildly alkaline solution, only a small amount of phosphate ion was adsorbed, regardless of the thermal treatment.
3.4. Applicability of thermally treated activated carbon for recovery of phosphate ion

Recovery of phosphate ion through temperature swing was again performed by using AC-1273K-3h, and its reusability was also tested (Fig. 9). For the first use, the amount of phosphate ion recovered by temperature swing was 0.0086 mmol g\(^{-1}\) (=0.82 mg g\(^{-1}\) as PO\(_4^{3-}\)), which corresponds to only 86% of the phosphate ion pre-adsorbed on it at 303 K. It should be noted that the recovery of phosphate ion was increased by repeated use and 99% of pre-adsorbed phosphate ion were recovered in the repeated reuses. This result demonstrates that the reusability and stability of the AC sample were successfully improved by the thermal treatment in a vacuum.

So far, the adsorption properties of the AC samples for phosphate ion have been investigated by using the aqueous solution prepared by dissolving KH\(_2\)PO\(_4\) in distilled water. However, actual wastewater contains various anionic chemicals other than phosphate ion. Co-existing chemicals in wastewater must affect the adsorption of phosphate ion on AC. Especially, anions like Cl\(^-\), NO\(_3^-\), and SO\(_4^{2-}\) are expected to have a negative impact on the adsorption of phosphate ion due to competitive adsorption. Thus, the adsorption properties of AC-Naca-CocoShe and AC-1273K-3h were evaluated in an aqueous solution containing chloride (Cl\(^-\)), nitrate (NO\(_3^-\)), and sulfate (SO\(_4^{2-}\)), in addition to phosphate ion, in equal concentrations (1 mmol
Table 3 summarizes the amounts of anions adsorbed on AC-Nava-CocoShe and AC-362K-3h at 303 K and 24 h, and the selectivity for phosphate ion (S\text{phosphate}), defined as

\[ S_{\text{phosphate}}(\%) = \frac{Q_{\text{phosphate}}}{Q_{\text{phosphate}} + Q_{\text{chloride}} + Q_{\text{nitrate}} + Q_{\text{sulfate}}} \times 100 \]  

(5)

where \( Q_{\text{phosphate}} \), \( Q_{\text{chloride}} \), \( Q_{\text{nitrate}} \), and \( Q_{\text{sulfate}} \) are the adsorbed amounts of each anion (mmol g\(^{-1}\)).

Even in the mixed aqueous solution, both the ACs adsorbed phosphate ion at 303 K. However, the amounts of adsorbed phosphate ion were only one third of those evaluated in the pure aqueous solution of phosphate ion. The thermal treatment had no effect on \( S_{\text{phosphate}} \), which was 19\% regardless of the thermal treatment. Improvement in the selectivity for phosphate ion is one of the future challenges for adsorption of phosphate ion by ACs.

4. Conclusions

In the present study, we attempted recovery of phosphate ion from an aqueous solution with commercial ACs by using the temperature swing method. Among the ACs, the one made from coconut shells and manufactured by Nakarai Tesque Inc. was the best adsorbent, and 73\% of phosphate ion was successfully recovered from the aqueous solution with 1.0 mmol L\(^{-1}\) of phosphate ion, but the performance was significantly degraded with repeated uses.
High-temperature thermal treatment of the AC in a vacuum effectively improved the adsorption capacity and recovered amount of phosphate ion owing to the elimination of oxygen-containing functional groups from the AC. The AC obtained by the thermal treatment under optimal conditions (1373 K and 3 h) showed an approximately 1.7-fold increase in the recovered amount of phosphate ion comparing with the untreated AC. Thermal treatment also improved the reusability of the AC, which was reusable at least three times without any severe loss of performance.

Phosphate ion was adsorbed onto basic sites of ACs via electrostatic interaction between negatively charged phosphate ion and positively charged basic site, which was mediated by protons.

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Declaration of Competing Interest

There is no potential conflict of interests to disclose.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/XXXXX

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[38] A. Drenkova-Tuhtan, K. Mandel, A. Paulus, C. Meyer, F. Mutter, C. Gellermann, G. Sextl,


<table>
<thead>
<tr>
<th>Sample</th>
<th>Manufacturer</th>
<th>Product name</th>
<th>Raw material</th>
<th>Surface area$^a$</th>
<th>Ash content$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-Naca-CocoShe</td>
<td>Nacalai Tesque, Inc.</td>
<td>Charcoal Activated</td>
<td>Coconut shell</td>
<td>1281</td>
<td>1.1</td>
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<tr>
<td>AC-Kura-CocoShe(GW)</td>
<td>Kuraray Chem. Co., Ltd.</td>
<td>Kuraray Coal™ GW</td>
<td>Coconut shell</td>
<td>890</td>
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<td>Kuraray Coal™ P-60</td>
<td>Coconut shell</td>
<td>1459</td>
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<td>Wako Pure Chem. Ind., Ltd.</td>
<td>Charcoal, Activated, Powder</td>
<td>Coconut shell</td>
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<td>AC-Kura-CocoShe</td>
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<td>Kuraray Coal™ GWC-H</td>
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<td>Charcoal Activated, granular</td>
<td>Coal</td>
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<td>AC-Naca-Sawd</td>
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<td>Charcoal Activated, powder</td>
<td>Sawdust</td>
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<td>AC-MCEvo-PetroRe</td>
<td>MC Evolve Technol. Co.</td>
<td>Maxsorb®</td>
<td>Petroleum resin</td>
<td>3054</td>
<td>0.2</td>
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</tbody>
</table>

$^a$BET surface area was estimated from N$_2$ adsorption isotherm taken at 77 K.

$^b$Ash content was estimated from weight of residue after combustion of activated carbon in air at 1123 K for 3 h.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment conditions</th>
<th>Surface area /m² g⁻¹</th>
<th>The numbers of sites a/mmol g⁻¹</th>
<th>pHb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp./K</td>
<td>Time/h</td>
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<td>acidic</td>
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<tr>
<td>AC-Naca-CocoShe</td>
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<td>AC-1073K-3h</td>
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<td>3</td>
<td>1250</td>
<td>0.22</td>
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<tr>
<td>AC-1273K-12h</td>
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<td>12</td>
<td>1203</td>
<td>0.08</td>
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</tbody>
</table>

a The numbers of acidic and basic sites were estimated by Boehm titration.

b Activated carbon (0.1 g) was dispersed in water (10 mL). After the suspension was stirred for 10 min, the pH of the suspension was measured.
Table 3

Adsorbed amounts of anions on AC-Naca-CocoShe and AC-1273K-3h measured in an aqueous solution containing PO$_4^{3-}$, Cl$^-$, NO$_3^-$, and SO$_4^{2-}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adsorbed amount/mmol g$^{-1}$</th>
<th>Selectivity for PO$_4^{3-}$ adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PO$_4^{3-}$</td>
<td>Cl$^-$</td>
</tr>
<tr>
<td>AC-Naca-CocoShe</td>
<td>0.010</td>
<td>0.002</td>
</tr>
<tr>
<td>AC-1273K-3h</td>
<td>0.016</td>
<td>0.004</td>
</tr>
</tbody>
</table>

*Conditions for adsorption: active carbon, 0.1 g; each anion, 1 mmol L$^{-1}$; volume of solution, 10 mL; temperature, 303 K; and time, 24 h.*
Fig. 1. Adsorbed amounts of phosphate ion on active carbons at (■) 303 K and (□) 373 K, and (■) difference in the adsorbed amount between 303 and 373 K. Conditions: active carbon, 0.1 g; 1 mmol L$^{-1}$ KH$_2$PO$_4$, 10 mL; and time, 24 h.
**Fig. 2.** Time-course change in the concentration of phosphate ion in solution for the removal and recovery of phosphate ion by using AC-Naca-CocoShe through temperature swing between 303 and 373 K. After 5 h of the adsorption at 303 K, the sample powder was separated by filtration and dried at 333 K overnight. Then, the sample powder was added to fresh distilled water, and the suspension was heated at 373 K to recover phosphate ion. (A) Adsorption of phosphate ion: AC-Naca-CocoShe, 5.0 g; 1 mmol L$^{-1}$ KH$_2$PO$_4$, 50 mL; and temperature, 303 K, (B) drying of the sample: in air at 333 K overnight, and (C) desorption of phosphate ion: distilled water, 25 mL; and temperature, 373 K.
Fig. 3. Repeated use of AC-Naca-CocoShe for recovery of phosphate ion by the temperature swing method. The experimental conditions for the adsorption and recovery of phosphate ion were the same as those for the experiment shown in Fig. 2.
Fig. 4. Influence of thermal treatment temperature for AC-Naca-CocoShe on the adsorption property for phosphate ion. Amount of adsorbed phosphate ion over activated carbons at (■) 303 K and (□) 373 K, and (■) difference in the adsorbed amount between 303 and 373 K. AC-Naca-CocoShe was thermally treated in a vacuum at 1073, 1273, or 1373 K for 3 h. Conditions: activated carbon, 0.1 g; 1 mmol L⁻¹ KH₂PO₄, 10 mL; and time, 24 h.
Fig. 5. Influence of thermal treatment duration for AC-Naca-CocoShe on the adsorption property for phosphate ion. Amount of adsorbed phosphate ion over activated carbons at (■) 303 K and (□) 373 K, and (■) difference in the adsorbed amount between 303 and 373 K. AC-Naca-CocoShe was thermally treated in a vacuum at 1273 K for 1, 3, 6, or 12 h. Conditions: activated carbon, 0.1 g; 1 mmol L⁻¹ KH₂PO₄, 10 mL; and time, 24 h.
Fig. 6. Adsorption isotherms of phosphate ion over (●) AC-Naca-CocoShe and (○) AC-1273K-3h at 303 K. AC-1273K-3h was obtained by thermal treatment of AC-Naca-CocoShe in a vacuum at 1273 K for 3 h. Conditions: activated carbon, 0.05 g; 0.3 ~20 mmol L⁻¹ KH₂PO₄, 5 mL, time, 24 h; and temperature, 303 K.
Fig. 7. Relationship between the number of basic sites on activated carbons and the amount of adsorbed phosphate ion at 303 K. The activated carbons in Table 2 were used to make the graph. (1) AC-Naca-CocoShe, (2) AC-1073K-3h, (3) AC1273K-3h, (4) AC-1373K-3h, (5) AC-1273K-1h, (6) AC-1273K-6h, and (7) AC-1273-12h.
Fig. 8. Proposed model for adsorption of phosphate ion on activated carbon. (a) Adsorption of phosphate ion through electrostatic interaction with delocalized π electrons on a graphene sheet and (b) strongly adsorbed phosphate ion interacting with oxygen-containing functional groups at the edge of and defects in a graphene sheet.
Fig. 9. Repeated use of AC-1273K-3h for recovery of phosphate ion by the temperature swing method. The experimental conditions for the adsorption and recovery of phosphate ion were the same as those for the experiment shown in Fig. 2.