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

5

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20 **ABSTRACT**

21 In the present study, we tested nine commercially available activated carbons for their abilities to
22 recover phosphate ion from an aqueous solution by a temperature swing method, in which
23 phosphate ion was adsorbed at 303 K, followed by desorption and recovery in pure water at 373
24 K. While the activated carbon made from coconut shell and manufactured by Nakarai Tesque Inc.
25 (trade name: Charcoal Activated) had a moderate adsorption capacity at 303 K, little amount of
26 phosphate ion was adsorbed on it at 373 K, meaning that it was an appropriate adsorbent for the
27 temperature swing method. Since the adsorbed amounts of phosphate ion for various activated
28 carbons at 303 K were correlated with the number of basic sites on them and were significantly
29 increased as pH of the solution decreased, it is presumed that phosphate ion was adsorbed on the
30 basic sites of the activated carbons with electrostatic interaction mediated by protons. High-
31 temperature thermal treatment of the activated carbon in a vacuum increased the recovered
32 amount of phosphate ion. This increase was brought about by elimination of oxygen-containing
33 functional groups from the activated carbon. By using activated carbon obtained by the thermal
34 treatment at 1273 K for 3 h, 86% of phosphate ion was recovered from an aqueous solution with
35 1.0 mmol L⁻¹ of phosphate ion through the temperature swing between 303 and 373 K. The

36 thermally treated activated carbon was reusable at least three times without any severe

37 performance loss.

38

39 Keywords:

40 Phosphate recovery; adsorption; activated carbon; temperature swing; thermal treatment

41

42 **1. Introduction**

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

50 Most of the phosphorus compounds used in fertilizer and other chemicals are produced
51 commercially from phosphate rock. However, since phosphate rock is a non-renewable resource
52 and the demand for it is expected to undergo rapid growth, future depletion of the phosphorus
53 supply is a concern [5-7]. In addition to the issue of resource depletion, phosphate causes
54 eutrophication in lakes, ponds, and bays, if domestic sewage, municipal wastewater, and
55 agricultural runoff are discharged into the environment without appropriate treatment [8]. Thus,
56 a system to effectively recover phosphate ion from effluent is urgently needed for sustainable
57 phosphorus procurement and aquatic conservation [6,9-12].

58 While the recovery of phosphate ion by crystallization of magnesium ammonium phosphate
59 hexahydrate and hydroxyapatite in wastewater has been studied extensively [13-20], recently,
60 adsorption over adsorbents for the recovery of phosphate ion has also been investigated
61 intensively especially for water containing low concentration phosphate ion [21-27]. Various
62 adsorbents and anion exchangers including granular ferric hydroxide [28], lanthanum hydroxide
63 [29], magnetite/lanthanum hydroxide hybrid [30], zirconium-containing solid materials [31-34],
64 double-layered hydroxides [35-38] were found to show high adsorption capacity for phosphate
65 ion. However, a large volume of regeneration solution is necessary to decompose the formed
66 metal phosphates for the crystallization method or to strip phosphate ion off adsorbents to recover
67 it, and these are major disadvantages of these methods.

68 As a method for recovery of phosphate ion with adsorbents, an adsorption-desorption cycle by
69 temperature swing, in which adsorption and desorption of phosphate ion are performed at
70 different temperatures, has been proposed. Ideally, this method, which is called a temperature
71 swing method here, does not need any regenerating solution, while heating the adsorbent is
72 necessary to provoke the desorption of phosphate ion. Thus, the temperature swing method is
73 potentially environmentally benign for the recovery of phosphate ion. Gotoh et al. developed a

74 thermosensitive gel adsorbent and applied it to the recovery of phosphate ion by the temperature
75 swing method [39]. The gel adsorbent synthesized by copolymerization of N-isopropylacrylamide
76 with N-[3-(dimethylamino)propyl]acrylamide has a specific volume phase transition temperature,
77 at which its hydrophobicity-hydrophilicity changes drastically. Below the volume phase transition
78 temperature, the gel swells in water due to its hydrophilic nature, and thus phosphate ion is
79 incorporated into the gel. After the incorporation of phosphate ion, the temperature of the gel is
80 increased above the volume phase transition temperature for it to release phosphate ion. However,
81 handling of the gel adsorbent is too difficult for practical application, especially with a
82 commercial-scale plant, because changes in the volume of the gel adsorbent through the
83 adsorption-desorption cycle are too large, owing to the volume phase transition, making the
84 operation difficult. In addition, the gel adsorbent is too soft to be used in conventional
85 commercial-scale plants.

86 Since adsorption over a common solid surface is often exothermic with a decrease in entropy,
87 Gibbs free energy of adsorption is increased as the temperature increases [40]. Thus, it is possible
88 that the adsorption capacity of an adsorbent is decreased as the temperature increases. Accordingly,
89 we hypothesized that phosphate ion could be recovered from solutions by the temperature swing

90 method even over conventional adsorbents. Activated carbons (ACs) are commonly used
91 adsorbents for water and air purifications, adsorption-separation processes, decoloration, and so
92 on [41-44]. Removal of phosphate ion from the solution by the adsorption on activated carbons
93 and related compounds has been investigated [45-48], but desorption (elution) of phosphate ion
94 from them have not been intensively concerned so far. In the present study, we applied commercial
95 ACs to the recovery of phosphate ion from an aqueous solution by the temperature swing method.
96 In addition, thermal treatment of AC was investigated to increase its adsorption capacity for
97 phosphate ion. An adsorption model for phosphate ion on AC was discussed based on the
98 adsorption isotherms and dependence of the adsorbed amount on the pH of the solution.

99

100 **2. Experimental**

101 *2.1. Activated carbon samples and thermal treatment*

102 Commercial AC samples used in this study are listed in Table 1 along with surface area and
103 ash content. Granular AC was crushed in a mortar to obtain a powdered sample. Prior to use, AC
104 was pretreated in boiling water to remove water-soluble impurities as follows. Powdery AC (3 g)
105 was added to distilled water (50 mL), and the suspension was heated with vigorous stirring at

106 reflux temperature for 24 h. After cooling down to room temperature, the AC was recovered by
107 filtration, washed with distilled water several times, and then dried at 373 K overnight.

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

118

119 2.2. Characterization

120 The surface area of AC was estimated by applying the Brunauer–Emmett–Teller (BET)
121 equation to an adsorption isotherm of N₂ measured at 77 K, which was acquired on a Belsorp-

122 mini instrument (BEL Japan Inc.). Before the measurement, AC was pretreated in a stream of N₂
123 at 473 K for 3 h. To determine ash content, AC was heated in air at 1123 K for 3 h to clear off
124 combustible matter. In this study, the residual matter after the combustion was regarded as ash.
125 The carbon content of AC was analyzed by using an elemental analyzer (ECS 4010; Costech
126 Instruments).

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

136 The pH of the aqueous suspension in which powdery AC was dispersed was measured to
137 evaluate the acidity or basicity on the AC surface. The aqueous suspension (10 mL) containing

138 0.1 g of AC was stirred for 10 min, and the pH of the suspension was measured by using a pH
139 meter (Metrohm, Model 827 pH lab).

140 A temperature-programmed desorption (TPD) profile for AC-Naca-CocoShe was measured
141 by using a Multitask TPD system equipped with a mass spectrometer. After the sample was
142 pretreated in a flow of He at 403 K for 1 h, the temperature of the sample was raised to 1273 K at
143 a rate of 10 K min⁻¹ with monitoring the signals of $m/e = 18, 28,$ and 44, which correspond to
144 H₂O, CO, and CO₂, respectively.

145

146 *2.3. Adsorption experiment for phosphate ion over activated carbons*

147 An aqueous solution of KH₂PO₄ (Wako Pure Chem. Ind. Ltd., 1.0 mmol L⁻¹, pH 5.1) was used
148 for the adsorption experiments. As the abundance ratio of phosphate ions under equilibrium
149 conditions calculated from the equilibrium constants shows (Fig. S1 in Supporting Information),
150 H₂PO₄⁻ was the predominant species in the solution with pH 5.1. The solution (10 mL) and AC
151 (0.1 g) were added to a test tube, and the resulting suspension was vigorously stirred at 303 K. A
152 small portion was withdrawn from the suspension at 24 h, followed by centrifugation to separate
153 AC. The concentration of phosphate ion in the supernatant was determined by using an ion

154 chromatograph (Tosoh Co. Ltd., IC-2001) with a column (TSK gel Super IC-AZ, Tosoh) and an
155 electrical conductivity detector. A mixed aqueous solution of NaHCO_3 (2.9 mmol L^{-1}) and
156 Na_2CO_3 (3.1 mmol L^{-1}) was used as eluting solution. The adsorbed amount of phosphate ion on
157 AC at a certain time was calculated according to eq. 1:

158
$$Q = \frac{C_0 - C_t}{M} V \quad (1)$$

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

163 An adsorption isotherm of phosphate ion on AC was measured at 303 K by changing the initial
164 concentration of KH_2PO_4 over a range of 0.5 to 20 mmol L^{-1} , while the adsorption time was fixed
165 at 24 h. In addition, effect of dose of AC on the adsorption of phosphate ion was investigated at
166 303 K by changing the amount of AC added to an aqueous solution of KH_2PO_4 (1.0 mmol L^{-1} ,
167 10 mL) over a range of 0.1 to 1.0 g, while the adsorption time was fixed at 24 h.

168

169 *2.4. Recovery of phosphate ion through temperature swing with activated carbon*

170 First, AC (5.0 g) was added to an aqueous solution of KH_2PO_4 (50 mL, 1.0 mmol L^{-1}), and
171 the suspension was stirred vigorously at 303 K. After 5 h, AC was taken out from the suspension
172 by filtration, and the concentration of phosphate ion in the filtrate was measured. The AC was
173 dried in an oven at 333 K overnight.

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

181

182 **3. Results and discussion**

183 *3.1. Adsorption and recovery of phosphate ion over activated carbon*

184 Fig. 1 shows the adsorbed amounts of phosphate ion over various ACs at 303 and 373 K for
185 24 h, which are denoted as $Q_{303\text{K}}$ and $Q_{373\text{K}}$, respectively. The amounts calculated by subtracting

186 Q_{373K} from Q_{303K} , which is denoted as M_{diff} , are also shown in Fig. 1. M_{diff} corresponds to the
187 amount of potentially recoverable phosphate ion by the temperature swing between 303 and 373
188 K. When M_{diff} is negative, it is given as zero in Fig. 1. Adsorption properties were substantially
189 different depending on the ACs. Except for AC-Naca-Sawd and AC-MCEvo-PetroRe, M_{diff} was
190 positive, indicating that recovery of phosphate ion from the solution was possible by the
191 temperature swing. While AC-Naca-Coal had the largest Q_{303K} , which was $0.057 \text{ mmol g}^{-1}$ ($= 5.4$
192 mg g^{-1} as PO_4^{3-}), Q_{373K} was also the largest among the AC samples. Thus, M_{diff} of AC-Naca-Coal
193 was moderate. In contrast, Q_{303K} was not so large for AC-Naca-CocoShe, but Q_{373K} was negligible,
194 resulting in the largest M_{diff} ($= 0.029 \text{ mmol g}^{-1} = 2.8 \text{ mg g}^{-1}$ as PO_4^{3-}) among the ACs. Thus, we
195 further investigated AC-Naca-CocoShe for the recovery of phosphate ion.

196 Because adsorption is a phenomenon occurring on a solid surface, it is expected that
197 adsorbed amounts of phosphate ion are correlated with surface areas of ACs. However, there was
198 no clear correlation between adsorption capacity and surface area (Fig. S2 in Supporting
199 Information). Another factor that is likely to affect the adsorption capacity is ash content, because
200 the ash in AC is commonly sodium and calcium oxides or hydroxide, which can form phosphorus
201 salts by reacting with phosphate ion. However, no correlation between the adsorption capacities

202 and ash content was observed (Fig. S3 in Supporting Information). Therefore, it was suggested
203 that acidic and basic sites on ACs were involved in the adsorption of phosphate ion over ACs.
204 This will be discussed in detail later.

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

211 Fig. 2 shows the results for the recovery of phosphate ion through the temperature swing
212 between 303 and 373 K over AC-Naca-CocoShe. First, phosphate ion was adsorbed on AC-Naca-
213 CocoShe at 303 K (Fig. 2(A)). In a separate experiment, we confirmed that the adsorption of
214 phosphate ion reached near equilibrium at 5 h and thus we decided that the time for adsorption
215 was 5 h. At the time, 97% of phosphate ion was removed from the solution, at which AC-Naca-
216 CocoShe adsorbed $0.0097 \text{ mmol g}^{-1}$ ($=0.92 \text{ mg g}^{-1}$ as PO_4^{3-}) of phosphate ion. Then, AC-Naca-
217 CocoShe was separated from the suspension by filtration and dried (Fig. 2(B)). The resulting AC-

218 Naca-CocoShe was added to fresh distilled water and the temperature of the suspension was kept
219 at 373 K. It takes note that the fresh distilled water used for the desorption of phosphate ion was
220 half the volume of the aqueous solution for the adsorption in order to concentrate phosphate ion
221 for the recovery. The concentration of phosphate ion in the water was increased and reached to
222 1.46 mmol L⁻¹ at 4 h. With the temperature swing between 303 and 373 K, 73 % of phosphate ion
223 was successfully recovered.

224 We further investigated the reusability of AC-Naca-CocoShe for the recovery of phosphate
225 ion (Fig. 3). As already shown, 0.0097 mmol g⁻¹ (=0.92 mg g⁻¹ as PO₄³⁻) of phosphate ion was
226 adsorbed on AC-Naca-CocoShe at 303 K, and 73% of it was desorbed at 373 K for the first use.
227 For the first reuse, however, the adsorbed amount was decreased to 0.0065 mmol g⁻¹ (=0.62 mg
228 g⁻¹ as PO₄³⁻), and only 85% of it was desorbed at 373 K. The adsorbed amount was further
229 decreased to 0.0052 mmol g⁻¹ (=0.49 mg g⁻¹ as PO₄³⁻), and desorbed amount of phosphate ion at
230 373 K was only 0.0050 mmol g⁻¹ (=0.48 mg g⁻¹ as PO₄³⁻) for the second reuse, which corresponds
231 to only 71 % of the amount of phosphate ion recovered in the first use. This means that AC-Naca-
232 CocoShe had a problem for reuse. Since the surface area and total pore volume of AC-Naca-
233 CocoShe after the second reuse were almost the same as those of the fresh one (1281 m² g⁻¹ →

234 1293 m² g⁻¹ and 0.54 cm³ g⁻¹ → 0.55 cm³ g⁻¹), the decrease in the performance for the recovery
235 of phosphate ion might be caused by irreversible adsorption of phosphate ion. Improvement in
236 the reusability of AC-Naca-CocoShe was achieved by thermal treatment, which will be described
237 later.

238

239 3.2. Thermal treatment of AC-Naca-CocoShe in vacuum

240 Generally, ACs have various functional groups on the surface, and the type and amount have
241 great impacts on their adsorption properties [52-55]. We thus investigated thermal treatment of
242 AC-Naca-CocoShe to increase the recoverable amount of phosphate ion (M_{diff}) and to improve
243 the reusability. Fig. 4 shows influence of the temperature in the thermal treatment for AC-Naca-
244 CocoShe on $Q_{303\text{K}}$, $Q_{373\text{K}}$, and M_{diff} . Thermal treatment increased $Q_{303\text{K}}$. Treatment at 1273 K or
245 higher was especially effective at increasing $Q_{303\text{K}}$. $Q_{303\text{K}}$ for the sample treated at 1373 K (AC-
246 1373K-3h) was approximately double that of the parent AC-Naca-CocoShe. While $Q_{373\text{K}}$ was also
247 increased by thermal treatment, the increase in $Q_{303\text{K}}$ was more pronounced. As a result, M_{diff} was
248 enhanced by the thermal treatment. AC-1373K-3h had an M_{diff} of 0.048 mmol g⁻¹ (= 4.6 mg g⁻¹
249 as PO₄³⁻), which was approximately 1.7 times larger than that of the parent AC-Naca-CocoShe

250 (0.028 mmol g⁻¹ = 2.7 mg g⁻¹ as PO₄³⁻).

251 Next, optimization of the duration of the thermal treatment was investigated using AC-Naca-
252 CocoShe, while the temperature was fixed at 1273 K. The results are shown in Fig. 5. Q_{303K}, Q_{373K},
253 and M_{diff} were increased as the treatment time was extended, but the degree of the increment
254 slowed down for 3 h or longer. The sample obtained by treatment at 1273 K for 12 h, AC-1273K-
255 12h, had an M_{diff} of 0.039 mmol g⁻¹ (= 3.75 mg g⁻¹ as PO₄³⁻).

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

263
$$Q_e = \frac{Q_{\max}KC}{1+KC} \quad (2)$$

264 where C, Q_e, Q_{max}, and K are the equilibrium concentration (mmol L⁻¹), amount of adsorbed
265 phosphate ion at C (mmol g⁻¹), maximum adsorbed amount of phosphate ion (mmol g⁻¹), and

266 adsorption coefficient (L mmol^{-1}), respectively. It was found that Q_{max} for AC-1273K-3h (0.14
267 $\text{mmol g}^{-1} = 13 \text{ mg g}^{-1}$ as PO_4^{3-}) was about three times larger than that for AC-Naca-CocoShe
268 ($0.045 \text{ mmol g}^{-1} = 4.3 \text{ mg g}^{-1}$ as PO_4^{3-}). On the other hand, the adsorption coefficient for AC-
269 1273K-3h (1.1 L mmol^{-1}) was smaller than that for AC-Naca-CocoShe (3.9 L mmol^{-1}). The
270 decrease in the adsorption coefficient suggests that most adsorption sites formed by the thermal
271 treatment were different to those originally present on AC-Naca-CocoShe and had a weak affinity
272 for phosphate ion.

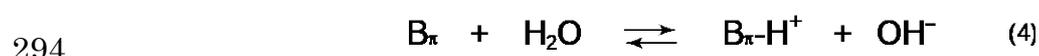
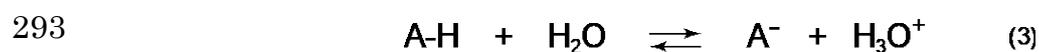
273

274 *3.3. Adsorption model for phosphate ion on activated carbon*

275 Normally, ACs have a graphite structure, consisting of graphene sheets in a stacked
276 arrangement. It is known that oxygen-containing functional groups, including carboxyl, lactone,
277 ether, phenolic hydroxyl, acid anhydride, and quinone groups, are present at the edges and carbon
278 vacancies in graphene sheets. Most of the oxygen-containing functional groups can be eliminated
279 by thermal treatment in a vacuum or inert atmosphere with the formation of CO, CO₂, and H₂O
280 [56]. For AC-Naca-CocoShe, the formations of CO and CO₂ were observed on the temperature-
281 programmed desorption (TPD) profile (Fig. S5), while H₂O formation was not pronounced over

282 the whole temperature range. In addition to the oxygen-containing functional groups, the
283 graphene sheet has delocalized π electrons that show basicity [57-59]. It is supposed that the acid
284 and base functions greatly influence the adsorption properties of ACs for phosphate ion in water.
285 Thus, we measured the numbers of acidic and basic sites on AC-Naca-CocoShe and samples
286 obtained by its thermal treatment.

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



295 Since the pH of the aqueous suspension of AC-Naca-CocoShe was 8.45, in spite of the number
296 of acidic sites being slightly larger than that of the basic ones, the reaction described by eq. 4 was
297 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
300 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,
303 the pH of the aqueous suspension with the AC sample was increased as the temperature and time
304 for the thermal treatment was increased. The trend in pH was consistent with the changes in the
305 numbers of acidic and basic sites with the thermal treatment. The carbon content involved in AC-
306 Naca-CocoShe was 91.2% and increased up to 98.0% and 99.6% for AC-1273K-3h and AC-
307 1373K-3h, respectively. The increase in the carbon content clearly indicated the elimination of
308 oxygen-containing functional groups. Through elimination, the carbonization of AC progressed
309 and consequently, more basic sites corresponding to delocalized π electrons were formed,
310 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
312 basic sites on AC-Naca-CocoShe and the samples obtained by the thermal treatment under
313 different conditions. The result shows that the amount of adsorbed phosphate ion was positively

314 correlated with the number of basic sites, suggesting that the basic sites on the AC samples were
315 deeply involved in the adsorption of phosphate ion. As mentioned above, protons formed by
316 reaction with water are present over the basic sites of AC (eq. 4), on which the protons presumably
317 interact with delocalized π electrons. Consequently, the surface of the AC was positively charged
318 in water if the basic sites are predominant, as in the AC samples obtained by thermal treatment.
319 On the other hand, phosphate ion was present mainly as HPO_4^{2-} in solution at pH of
320 approximately 8 (Fig. S1 in Supporting Information). Based on this, we propose models for the
321 adsorption of phosphate ion on the AC samples as shown in Fig. 8. Basically, phosphate ion
322 (HPO_4^{2-}) may interact electrostatically with H^+ over the basic site on the surface (Fig. 8(a)). In
323 addition to such interactions, phosphate ion may interact with oxygen-containing functional
324 groups at the edge of and defects in the graphene sheet through hydrogen bonding (Fig. 8(b)) if
325 they exist, like in AC-Naca-CocoShe, resulting in the strong adsorption of phosphate ion. We
326 presume that phosphate ion interacting with oxygen-containing functional groups may make a
327 covalent bond such as an ester (Fig. 8(b)), forming irreversibly adsorbed phosphate species that
328 never desorb, even at 373 K. That may cause a deterioration in the reusability of the untreated
329 AC-Naca-CocoShe (Fig. 3).

330 As Fig. 7 shows, the number of adsorbed phosphate ion in the AC samples at 303 K under
331 the present conditions was only about one tenth of the number of basic sites. All the AC samples
332 used in this study gave a type I adsorption isotherm for N₂ at 77 K (Fig. S6 in Supporting
333 Information), indicating that they were microporous materials. The size of micropores estimated
334 from the *t*-plot, which was calculated from the corresponding N₂ adsorption isotherms, were
335 about 0.8 nm for all the samples (Fig. S6 in Supporting Information). On the other hand, the
336 molecular size of the phosphate ion estimated on the basis of its structure is approximately 0.6
337 nm. Thus, it is possible for phosphate ion to enter micropores. In fact, a significantly large amount
338 of phosphate ion was adsorbed on Ac-Naca-CocoShe and AC-1273K-3h when the adsorption
339 experiment was carried out under low pH conditions (Fig. S7 in Supporting Information), while
340 pH under standard conditions was around 8, supporting the speculation mentioned above. As we
341 propose in Fig. 8, phosphate ion is adsorbed on basic sites of AC via electrostatic interactions
342 between phosphate ion and H⁺ on AC. Since the amount of H⁺ on AC was not so large under the
343 standard conditions due to the mildly alkaline solution, only a small amount of phosphate ion was
344 adsorbed, regardless of the thermal treatment.

345

346 *3.4. Applicability of thermally treated activated carbon for recovery of phosphate ion*

347 Recovery of phosphate ion through temperature swing was again performed by using AC-
348 1273K-3h, and its reusability was also tested (Fig. 9). For the first use, the amount of phosphate
349 ion recovered by temperature swing was $0.0086 \text{ mmol g}^{-1}$ ($=0.82 \text{ mg g}^{-1}$ as PO_4^{3-}), which
350 corresponds to only 86% of the phosphate ion pre-adsorbed on it at 303 K. It should be noted that
351 the recovery of phosphate ion was increased by repeated use and 99% of pre-adsorbed phosphate
352 ion were recovered in the repeated reuses. This result demonstrates that the reusability and
353 stability of the AC sample were successfully improved by the thermal treatment in a vacuum.

354 So far, the adsorption properties of the AC samples for phosphate ion have been
355 investigated by using the aqueous solution prepared by dissolving KH_2PO_4 in distilled water.
356 However, actual wastewater contains various anionic chemicals other than phosphate ion. Co-
357 existing chemicals in wastewater must affect the adsorption of phosphate ion on AC. Especially,
358 anions like Cl^- , NO_3^- , and SO_4^{2-} are expected to have a negative impact on the adsorption of
359 phosphate ion due to competitive adsorption. Thus, the adsorption properties of AC-Naca-
360 CocoShe and AC-1273K-3h were evaluated in an aqueous solution containing chloride (Cl^-),
361 nitrate (NO_3^-), and sulfate (SO_4^{2-}), in addition to phosphate ion, in equal concentrations (1 mmol

362 L⁻¹ each). Table 3 summarizes the amounts of anions adsorbed on AC-Nava-CocoShe and AC-
363 1273K-3h at 303 K and 24 h, and the selectivity for phosphate ion ($S_{\text{phosphate}}$), defined as

$$364 \quad S_{\text{phosphate}}(\%) = \frac{Q_{\text{phosphate}}}{Q_{\text{phosphate}} + Q_{\text{chloride}} + Q_{\text{nitrate}} + Q_{\text{sulfate}}} \times 100 \quad (5)$$

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

366 Even in the mixed aqueous solution, both the ACs adsorbed phosphate ion at 303 K. However,

367 the amounts of adsorbed phosphate ion were only one third of those evaluated in the pure aqueous

368 solution of phosphate ion. The thermal treatment had no effect on $S_{\text{phosphate}}$, which was 19%

369 regardless of the thermal treatment. Improvement in the selectivity for phosphate ion is one of the

370 future challenges for adsorption of phosphate ion by ACs.

371

372 **4. Conclusions**

373 In the present study, we attempted recovery of phosphate ion from an aqueous solution with

374 commercial ACs by using the temperature swing method. Among the ACs, the one made from

375 coconut shells and manufactured by Nakarai Tesque Inc. was the best adsorbent, and 73% of

376 phosphate ion was successfully recovered from the aqueous solution with 1.0 mmol L⁻¹ of

377 phosphate ion, but the performance was significantly degraded with repeated uses.

378 High-temperature thermal treatment of the AC in a vacuum effectively improved the
379 adsorption capacity and recovered amount of phosphate ion owing to the elimination of oxygen-
380 containing functional groups from the AC. The AC obtained by the thermal treatment under
381 optimal conditions (1373 K and 3 h) showed an approximately 1.7-fold increase in the recovered
382 amount of phosphate ion comparing with the untreated AC. Thermal treatment also improved the
383 reusability of the AC, which was reusable at least three times without any severe loss of
384 performance.

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

388

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393

394 **Declaration of Competing Interest**

395 There is no potential conflict of interests to disclose.

396

397 **Appendix A. Supplementary material**

398 Supplementary data to this article can be found online at [https:// doi.org/10.1016/XXXXXX](https://doi.org/10.1016/XXXXXX)

399

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Table 1

Activated carbons used in this study

Sample	Manufacturer	Product name	Raw material	Surface area ^a /m ² g ⁻¹	Ash content ^b /wt.%
AC-Naca-CocoShe	Nacalai Tesque, Inc.	Charcoal Activated	Coconut shell	1281	1.1
AC-Kura-CocoShe(GW)	Kuraray Chem. Co., Ltd.	Kuraray Coal™ GW	Coconut shell	890	0.8
AC-Kura-CocoShe(P-60)	Kuraray Chem. Co., Ltd.	Kuraray Coal™ P-60	Coconut shell	1459	0.2
AC-Kura-CocoShe(GC)	Kuraray Chem. Co., Ltd.	Kuraray Coal™ GC	Coconut shell	1316	0.3
AC-Wako-CocoShe	Wako Pure Chem. Ind., Ltd.	Charcoal, Activated, Powder	Coconut shell	1100	0.8
AC-Kura-CocoShe	Kuraray Chem. Co., Ltd.	Kuraray Coal™ GWC-H	Coal	1126	3.0
AC-Naca-Coal	Nacalai Tesque, Inc.	Charcoal Activated, granular	Coal	859	7.6
AC-Naca-Sawd	Nacalai Tesque, Inc.	Charcoal Activated, powder	Sawdust	1091	3.9
AC-MCEvo-PetroRe	MC Evolve Technol. Co.	Maxsorb®	Petroleum resin	3054	0.2

^aBET surface area was estimated from N₂ adsorption isotherm taken at 77 K.^bAsh content was estimated from weight of residue after combustion of activated carbon in air at 1123 K for 3 h.

Table 2

Conditions for thermal treatment of AC-Naca-CocoShe and surface area, the numbers of acid and basic sites on the activated carbons, and pH of water in which activated carbon was dispersed.

Sample	Treatment conditions		Surface area /m ² g ⁻¹	The numbers of sites ^a /mmol g ⁻¹		pH ^b
	Temp./K	Time/h		acidic	basic	
AC-Naca-CocoShe	untreated		1281	0.33	0.31	8.45
AC-1073K-3h	1073	3	1250	0.22	0.41	8.67
AC-1273K-3h	1273	3	1238	0.10	0.62	9.03
AC-1373K-3h	1373	3	1230	0.08	0.74	9.70
AC-1273K-1h	1273	1	1242	0.10	0.59	8.89
AC-1273K-6h	1273	6	1211	0.09	0.63	9.01
AC-1273K-12h	1273	12	1203	0.08	0.66	9.11

^aThe numbers of acidic and basic sites were estimated by Boehm titration.

^bActivated 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-} ^a

Sample	Adsorbed amount/mmol g ⁻¹					Selectivity for PO_4^{3-} -adsorption /%
	PO_4^{3-}	Cl^-	NO_3^-	SO_4^{2-}	Total	
AC-Naca-CocoShe	0.010	0.002	0.035	0.005	0.052	19
AC-1273K-3h	0.016	0.004	0.053	0.013	0.086	19

^aConditions 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.

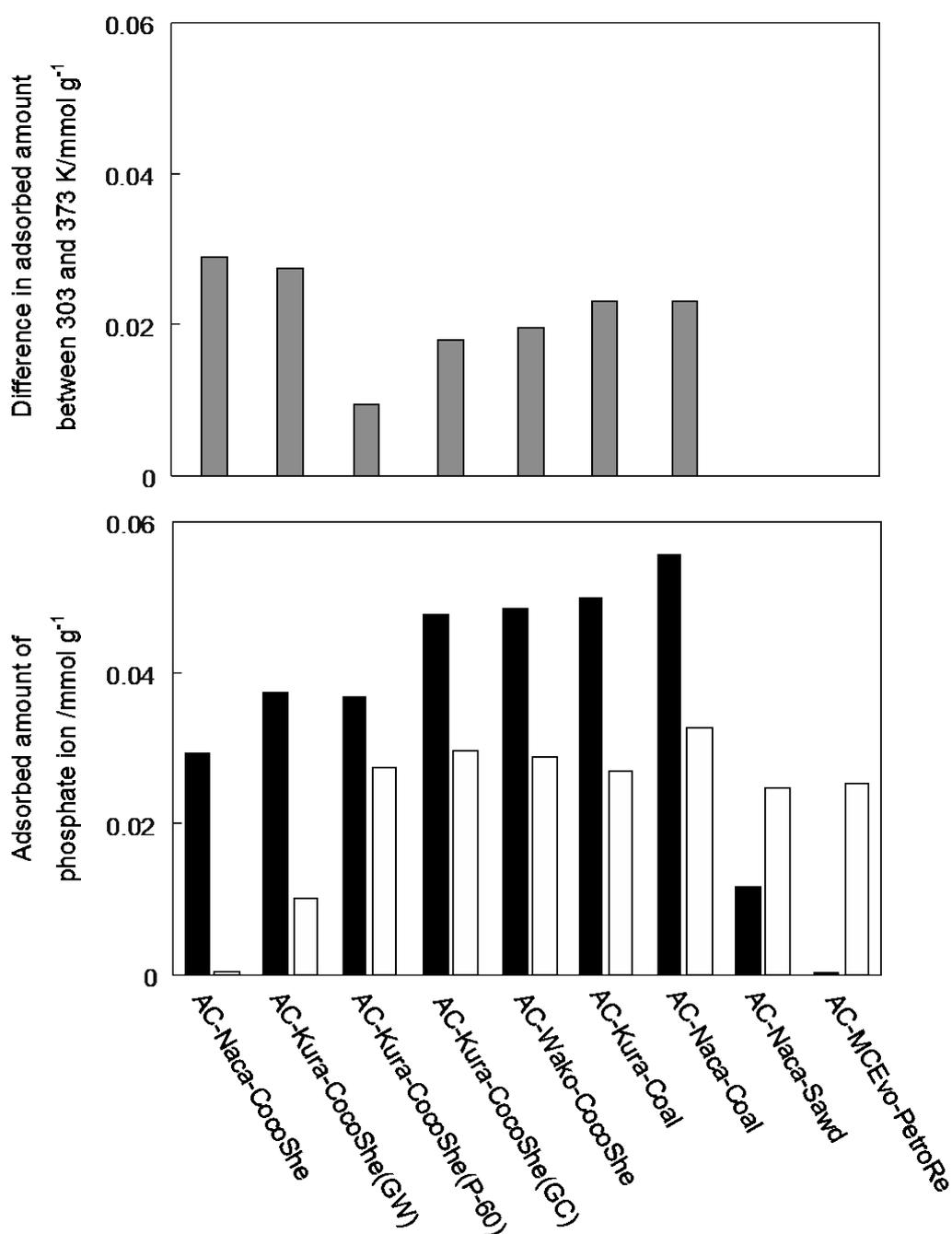


Fig. 1. Adsorbed amounts of phosphate ion on active carbons at (■) 303 K and (□) 373 K, and (■) difference in the adsorbed amount between 303 and 373 K. Conditions: active carbon, 0.1 g; 1 mmol L⁻¹ KH₂PO₄, 10 mL; and time, 24 h.

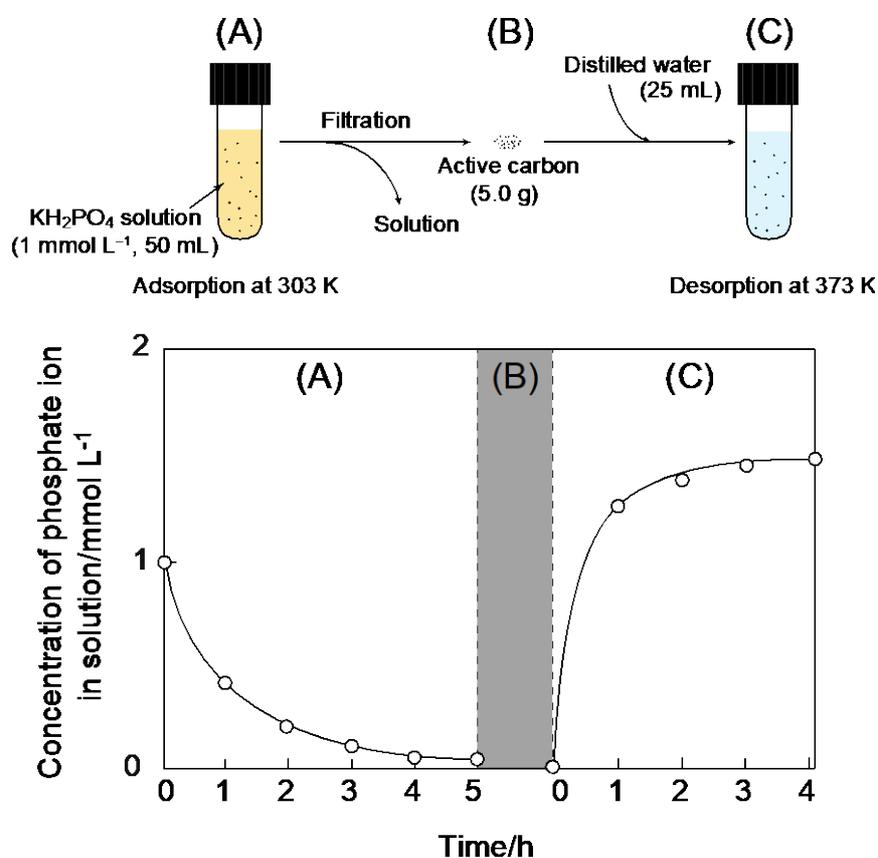


Fig. 2. Time-course change in the concentration of phosphate ion in solution for the removal and recovery of phosphate ion by using AC-Naca-CocoShe through temperature swing between 303 and 373 K. After 5 h of the adsorption at 303 K, the sample powder was separated by filtration and dried at 333 K overnight. 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_2PO_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.

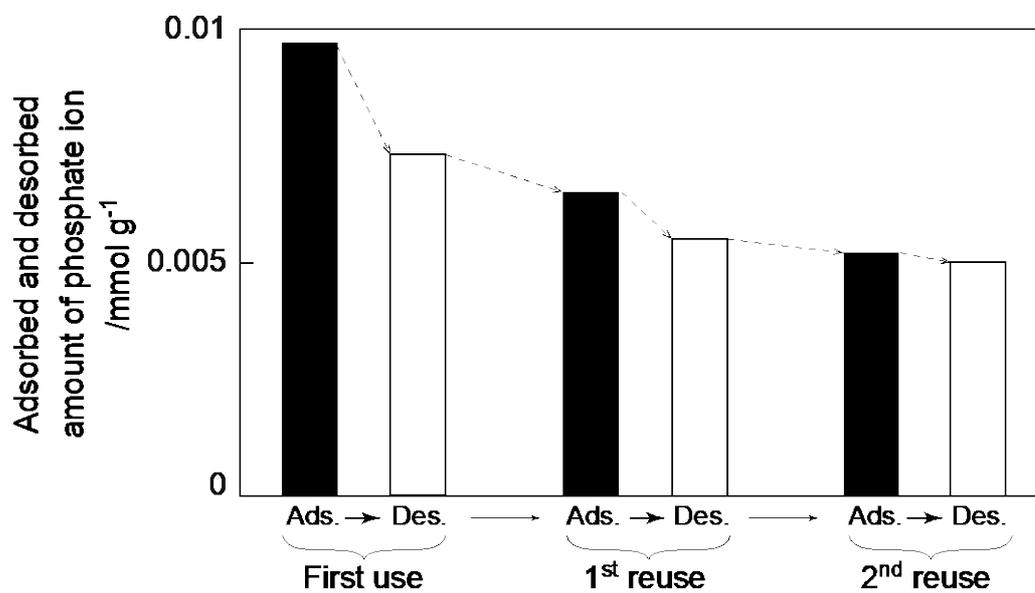


Fig. 3. Repeated use of AC-Naca-CocoShe for recovery of phosphate ion by the temperature swing method. The experimental conditions for the adsorption and recovery of phosphate ion were the same as those for the experiment shown in Fig. 2.

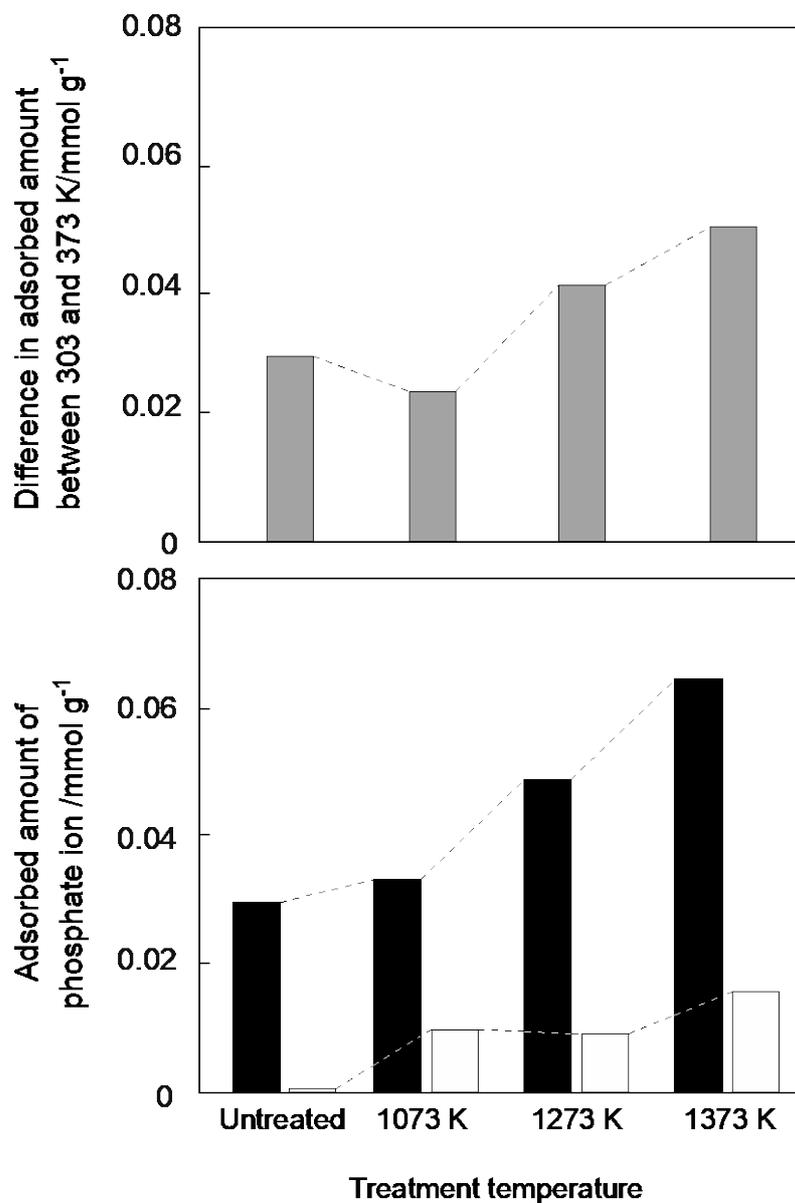


Fig. 4. Influence of thermal treatment temperature for AC-Naca-CocoShe on the adsorption property for phosphate ion. Amount of adsorbed phosphate ion over activated carbons at (■) 303 K and (□) 373 K, and (■) difference in the adsorbed amount between 303 and 373 K. AC-Naca-CocoShe was thermally treated 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.

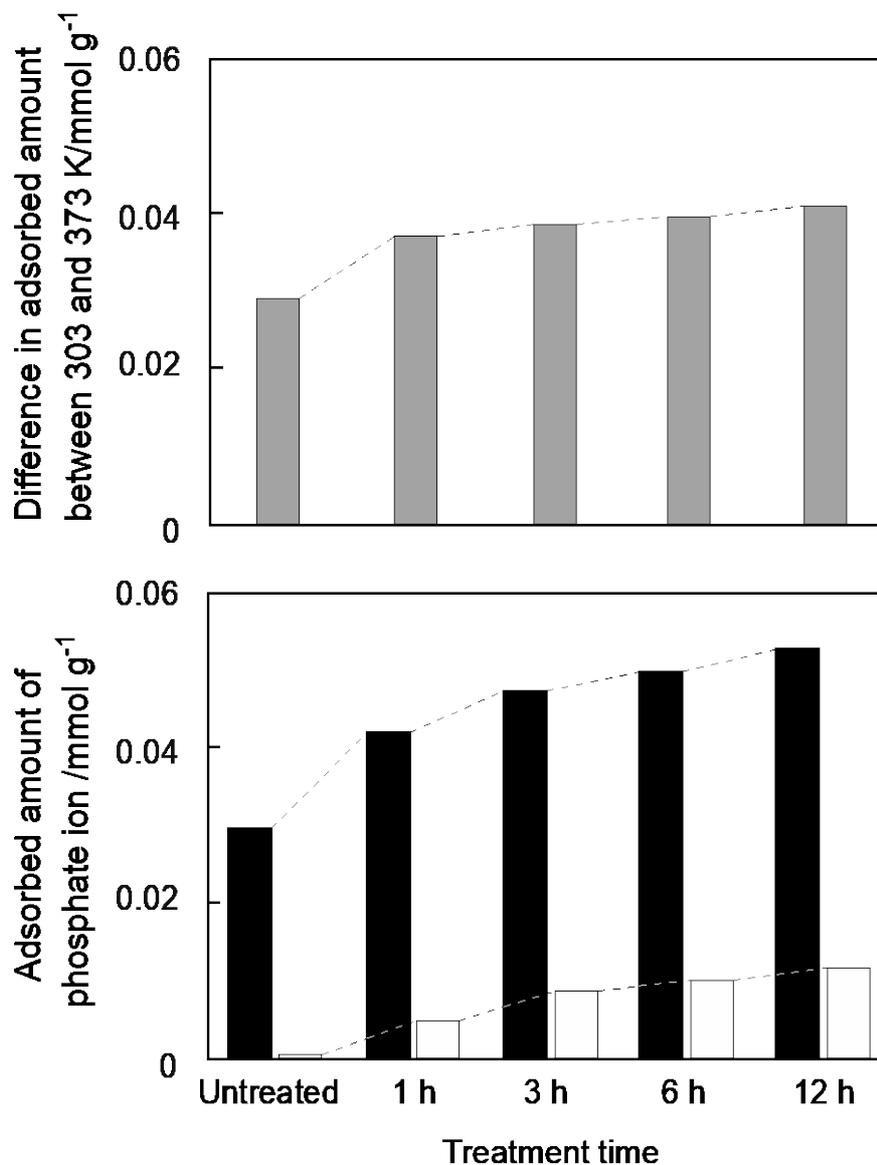


Fig. 5. Influence of thermal treatment duration for AC-Naca-CocoShe on the adsorption property for phosphate ion. Amount of adsorbed phosphate ion over activated carbons at (■) 303 K and (□) 373 K, and (■) difference in the adsorbed amount between 303 and 373 K. AC-Naca-CocoShe was thermally treated 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.

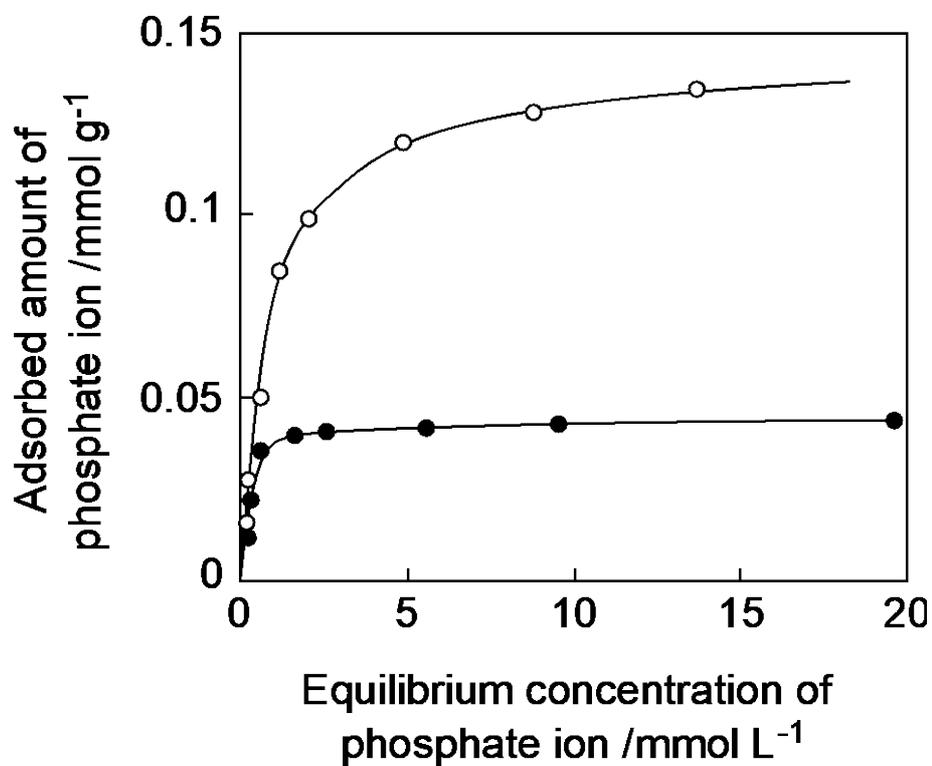


Fig. 6. Adsorption isotherms of phosphate ion over (●) AC-Naca-CocoShe and (○) AC-1273K-3h at 303 K. AC-1273K-3h was obtained by thermal treatment of AC-Naca-CocoShe in a vacuum at 1273 K for 3 h. Conditions: activated carbon, 0.05 g; 0.3 ~20 mmol L⁻¹ KH₂PO₄, 5 mL, time, 24 h; and temperature, 303 K.

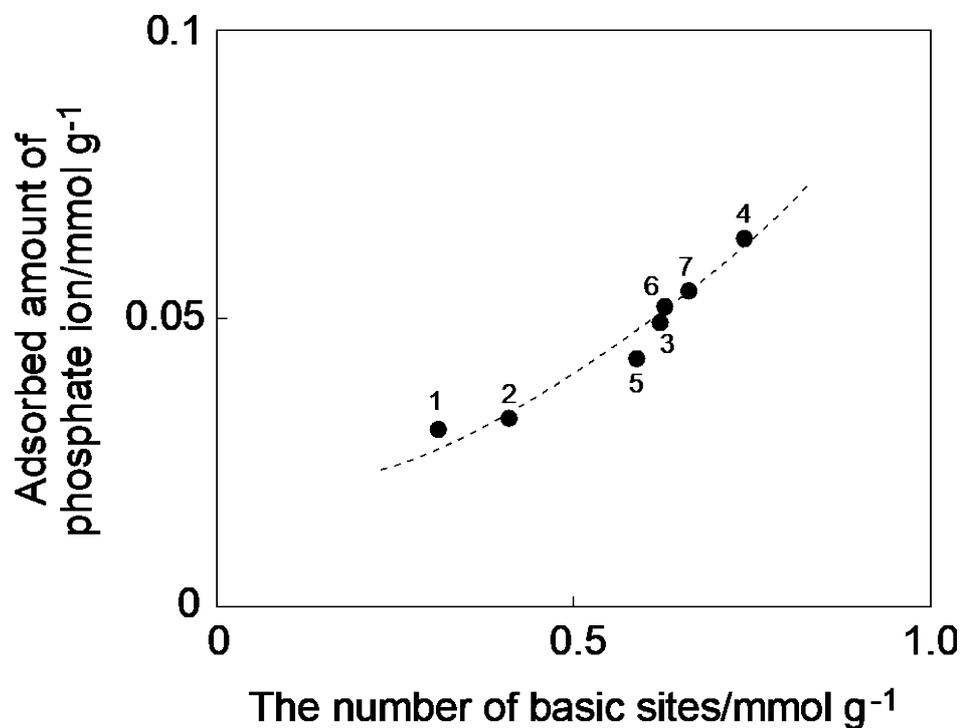


Fig. 7. Relationship between the number of basic sites on activated carbons and the amount of adsorbed phosphate ion at 303 K. The activated carbons in Table 2 were used to make the graph. (1) AC-Naca-CocoShe, (2) AC-1073K-3h, (3) AC1273K-3h, (4) AC-1373K-3h, (5) AC-1273K-1h, (6) AC-1273K-6h, and (7) AC-1273-12h.

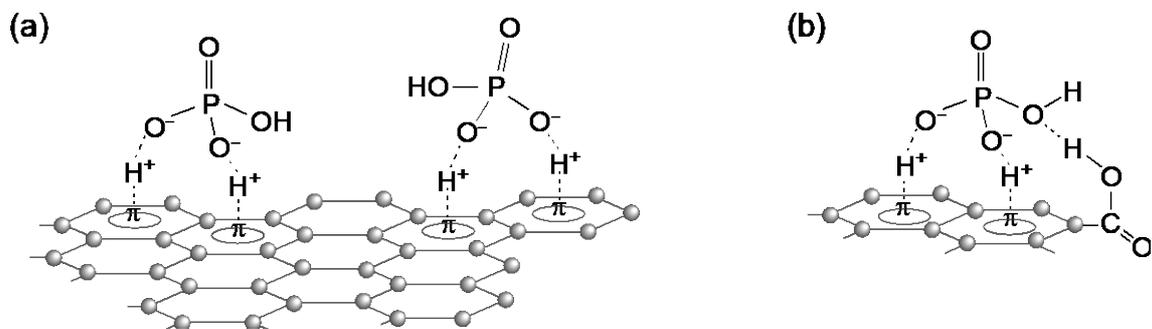


Fig. 8. Proposed model for adsorption of phosphate ion on activated carbon. (a) Adsorption of phosphate ion through electrostatic interaction with delocalized π electrons on a graphene sheet and (b) strongly adsorbed phosphate ion interacting with oxygen-containing functional groups at the edge of and defects in a graphene sheet.

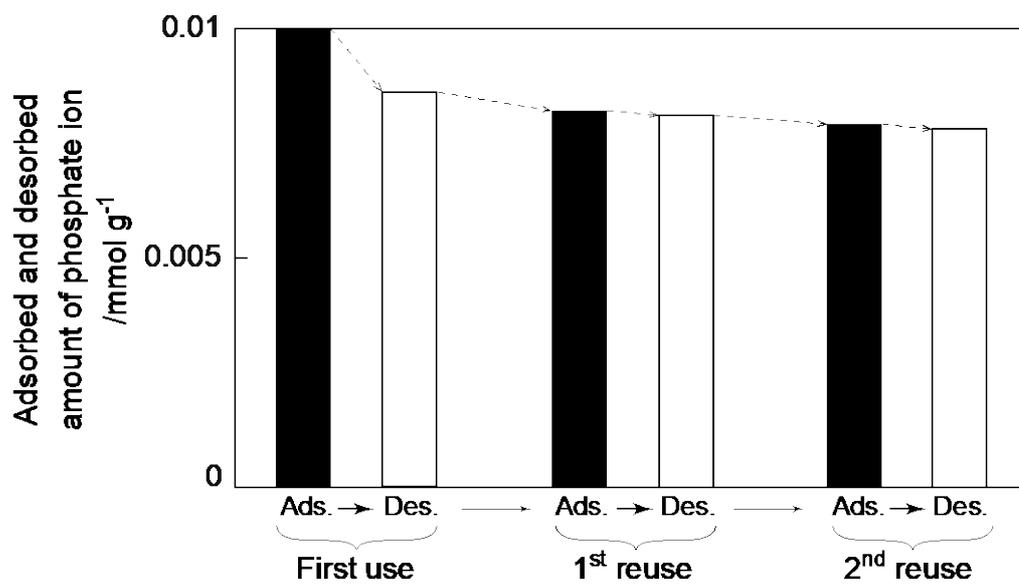


Fig. 9. Repeated use of AC-1273K-3h for recovery of phosphate ion by the temperature swing method. The experimental conditions for the adsorption and recovery of phosphate ion were the same as those for the experiment shown in Fig. 2.

