Phosphate ion adsorption properties of PAN-based activated carbon fibers prepared with K_2CO_3 activation

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Received: 30 October 2019 / Accepted: 10 March 2020 / Published online: 19 March 2020
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Abstract

Adsorbents for phosphate ion removal were prepared with K_2CO_3 activation and heat treatment at 950 °C from polyacrylonitrile-based carbon fiber (PAN-CF). Comparative tests for specific surface area and pore structures, elemental and nitrogen species analysis, and phosphate ion adsorption experiments demonstrated that K(3)-Δ, which was activated with K_2CO_3 /PAN-CF weight ratio of 3 and then treated at 950 °C, exhibited larger amount of quaternized-nitrogen (0.46 wt%) and equilibrium adsorption amount (0.23 mmol/g) among the prepared adsorbents. The experimental data for phosphate adsorption of K(3)-Δ was well fitted to Langmuir adsorption isotherms and pseudo-second-order kinetic model. As for regeneration performance, K(3)-Δ still remained more than 60% adsorption amount of the fresh adsorbent after rejuvenation treatment.

Keywords Polyacrylonitrile-based activated carbon fiber · Phosphate ion adsorption · K_2CO_3 activation · Quaternized-nitrogen · Adsorption mechanism · Regeneration

1 Introduction

Phosphorus (P) is one of the essential nutrients for animals and plants [1]. On the other hand, it causes water quality deterioration such as algal blooms and red tide through discharging phosphate and other nutrients into closed water area by daily human activities [2, 3]. The wastewater exhausted from houses, factories, fields, and farms contains a great amount of phosphorus exceeding the regulation. Chiba prefectural assembly, Japan, has made efforts so that farmers and livestock farmers should restrict dischargeable P concentration of less than 8 mg/L and encouraged the citizen to reduce nutrients in domestic wastewater in the Environmental White Paper of FY 2017. Lake Inba and Lake Tega were the first and second largest lake in Chiba prefecture, Japan [4], and their environmental standards of total phosphorus (TP) were

regulated less than 0.03 and 0.1 mg/L, respectively [5]. However, according to the Environmental White Paper of FY2017, the TP concentrations in both lakes obviously exceeded the standard values (0.14 and 0.15 mg/L, respectively), and they were reported to be the first and third worst eutrophic lake in Japan in 2016 by the Ministry of the Environment, Government of Japan [4]. The World Health Organization (WHO) also recommends phosphate ion concentration of less than 5 mg/L in natural water [6], though water blooms have broken out in China and South-east Asia frequently [1, 7, 8]. In order not to occur water environmental problems, it is important to not only reduce releasing nutrients into natural water but also remove phosphate from wastewater [9–11].

Generally, phosphate has been removed with coagulating sedimentation method at sewage treatment facility [6, 12]. The problems of this method were to produce a large

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amount of waste and not to be able to reuse the phosphorus resources. Although calcium superphosphate is produced from rock phosphorus with sulfuric acid as a low-cost phosphorus nutrient for crops, the rock phosphorus output has been decreasing year by year [13]. To solve these problems, adsorption method has been studied in order to remove P from environmental water and recycle as a nutrient [14–18].

Various adsorbents were widely investigated for phosphate removal, such as Ca and Mg modified adsorbent [19], Fe–Mn oxide [20], Fe–Al oxide [21], zeolite [22], Al-biochar [23], activated carbon [24], iron oxide coated activated carbon [25], and Ln-doped activated carbon [26]. Most of adsorbents were prepared with metal ions as adsorption site [27–29]. This preparation method could innovate high-performance adsorption ability for any material as well as metal ions such as Mg and Ca could be introduced onto its surface. However, there were also disadvantages such as their low adsorption capacities and the environmental damage due to releasing the surplus metals. Ion exchange resin is high cost to be purchased [30] and not robustness against heating conditions. In this study, adsorbents were prepared from frame-resistant polyacrylonitrile-based carbon fiber (PAN-CF), PYROMEX (PYR), with K_2CO_3 activation. In previous studies, the nitrogen contained in PAN-CF would be quaternized through heat treatment at over 500 °C [31, 32], and PAN-ACF treated at 950 °C had the maximum adsorption amount [33]. The positively charged quaternized-nitrogen (N-Q) could be effective adsorption site for phosphate anion. On the other hand, the negatively charged pyridine/pyrrole N-oxide (N-X) and oxygen functional groups might prevent phosphate ion from approaching onto the adsorbent surface. In order to obtain higher phosphate adsorption amount, both the more amount of nitrogen and the higher proportion of N-Q in the adsorbent are essential. Therefore, PYR should be activated mildly to remain the nitrogen adsorption site on the adsorbent.

In this study, K_2CO_3 was used as a chemical activator for developing the specific surface area and pore structures of PYR. Generally, the activators for chemical activation such as KOH [34], $ZnCl_2$ [35], and H_3PO_4 [36] have been studied widely to prepare high performance activated carbons from various raw materials. On the other hand, there are a few studies on K_2CO_3 activation method because K_2CO_3 shows less activation ability compared to KOH [37]. In our previous study, the KOH-activated PYR adsorbed phosphate ion of 0.1 mmol/g, though steam-activated PYR adsorbed 0.2 mmol/g [38]. The low adsorption amount of KOH-activated PYR would be caused by its low nitrogen content. KOH reacts with both carbon and nitrogen strictly causing the decrease in yield, specific surface area and pore structures. It is well known that KOH activation

is processed through some chemical reaction as follows [39, 40];

The Eq. (5) shows that K_2CO_3 also reacts with carbon and activates the material like KOH. When the activation process starts with K_2CO_3 , the raw material is activated through only Eqs. (2)–(5). It means that carbon and nitrogen react mildly with K_2CO_3 compared to KOH, leading to the restriction of nitrogen decrease. Moreover, K_2CO_3 is weaker basic chemical, so it damages the environment less than KOH.

2 Materials and methods

2.1 Materials

The adsorbent used in the experiments was prepared from polyacrylonitrile carbon fiber, PYROMEX (PYR), which was purchased from Toho Tenax Co., Ltd., Japan. The PYR contains 20.9 wt% nitrogen and has 7 m²/g specific surface area. All reagents such as potassium dihydrophosphate, hydrochloric acid, and potassium carbonate were purchased from Kanto Chemical Co., Ltd., Japan. Phosphate ion (PO_4^{3-}) stock solution (3 mmol/L) was prepared by dissolving KH_2PO_4 in deionized water.

2.2 Preparation for adsorbents

The PYR was dried in an oven at 110 °C for 1 h to remove the moisture. Approximately 3 g of dried-PYR was mixed with K_2CO_3 solid in a ceramic boat and heated up to 800 °C (10 °C/min) and then maintained at 800 °C for 30 min under N_2 gas flow using a horizontal tubular furnace. The weight ratio of K_2CO_3 /PYROMEX were 1, 2, 3, 4, and 5. The activated-PYR was washed using 1 mol/L HCl and hot distilled water. After drying in an oven at 110 °C for 24 h, the sample was heated up to 950 °C (10 °C/min) and then kept for 30 min to transform the nitrogen species into N-Q. The adsorbents were designated as K(x)-Δ, where x is the weight ratio of activator (K_2CO_3 /PYR). In order to compare with K(x)-Δ, PYR activated by K_2CO_3 (without heat

treatment at 950 °C) was also prepared and named as K(x) as a reference adsorbent.

2.3 Adsorption experiments

The adsorbents prepared at different activator ratios were compared each other for phosphate adsorption amount through batch experiments. After drying in oven at 110 °C for 1 h, approximately 30 mg of adsorbent and 15 mL of 3 mmol/L KH_2PO_4 solution were mixed in 30 mL conical flask and capped. The initial solution pH was around 4.7, and the solution pH was not adjusted before adsorption experiments, except for examining the effect of pH on phosphate adsorption. These flasks were placed in a thermostat shaker and agitated at 25 °C and 100 rpm for 24 h. In this study, the concentration of the phosphate ion (PO_4^{3-}) in the solution was determined by a UV-Vis spectrophotometer (Shimadzu UV-2550, Japan) using the molybdenum blue colorimetric method. The equilibrium adsorption amount (Q_e , mmol/g) was calculated from Eq. (6) [41];

$$Q_e = \frac{(C_0 - C_e)v}{m}, \quad (6)$$

where C_0 and C_e are the initial and equilibrium concentration (mmol/L), respectively, and v is the volume of the solution (L), and m is the weight of adsorbent (g).

2.4 Adsorption isotherm

Approximately 30 mg of adsorbent (K(3) or K(3)-Δ) and 15 mL of phosphate ion solution were added into a conical flask with different initial concentrations ranged from 0.1 to 10 mmol/L. These flasks were shaken at 25 °C with the speed of 100 rpm using thermostat shaker for 24 h. The concentration of phosphate ion in the agitated solution was determined by the same method mentioned in the Sect. 2.3. Adsorption isothermal properties were fitted by the Langmuir model. The maximum adsorption capacity (Q_m , mmol/g) and equilibrium adsorption affinity (K_e , L/mmol) were calculated from Eq. (7) [23];

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_e} \quad (7)$$

2.5 Adsorption kinetics

The equilibrium adsorption times were determined through the adsorption kinetics experiments. Approximately 150 mg of adsorbents (K(3) or K(3)-Δ) were impregnated into 75 mL of 3 mmol/L phosphate ion solution in a 200 mL conical flask. These flasks were capped and shaken at 25 °C with

the speed of 100 rpm using thermostat shaker for 24 h. The concentration of phosphate ion in the agitated solution was determined by the same method mentioned in the Sect. 2.3.

2.6 Characterization

Nitrogen adsorption/desorption (BELSORP-mini II, Microtrac BEL Co., Ltd.) at −196 °C was used to calculate the specific surface area and pore volume of mesopore (the pore diameter ranges in 2–50 nm) and micropore (less than 2 nm). Before analysis, the sample was outgassed at 300 °C for 1 h. The specific surface area (S_{BET}) was obtained by BET method. The total pore volume (V_{total}) and pore average diameter (D_{avg}) were calculated using nitrogen adsorption amount and S_{BET} , and micro pore volume (V_{micro}) was calculated by subtracting method using α_s plots [42]. The elemental contents of C, H, and N were determined using Perkin Elmer 2400 II (Perkin Elmer Japan Co., Ltd.). O content was calculated to subtract CHN amounts from 100 wt% because X-ray photoelectron spectroscopy analysis had detected only C, N, and O as elemental contains in PYR. The XPS measurement was conducted with the binding energy 392–408 eV to analyze the N functional species such as N-6 (398.6 ± 0.3 eV), N-5 (400.5 ± 0.3 eV), N-Q (401.3 ± 0.3 eV), and N-X (402–405 eV) [31].

2.7 Desorption experiments

One of the advantages using activated carbon for adsorption is the ability of regeneration and reuse. Regeneration of adsorbent was done with three desorption solutions such as HCl (0.5, 1, and 2 mol/L), NaCl (1 mol/L) or NaOH (1 mol/L). Moreover, in order to desorb phosphate ion from adsorbent completely, the adsorbent was heated up to 950 °C (10 °C/min) and then kept for 30 min. The adsorbent after adsorption experiments (following the method of Sect. 2.3) was filtered with filter paper and washed by distilled water. For desorption, the adsorbent was agitated in the chemical solution for 24 h at 25 °C and 100 rpm. After that, the desorption solution was decanted, and the adsorbent was washed with hot distilled water using Soxhlet extractor until solution pH 5 was established. As for heating method, the washed adsorbent was dried in an oven at 110 °C overnight, and then inserted into tubular furnace. During the heat treatment, N_2 gas continuously flowed at 100 mL/min, and the temperature was fixed at 950 °C for 30 min.

Fig. 1 The equilibrium phosphate adsorption amount of K(x) and K(x)-Δ (x is the weight ratio of K₂CO₃ to PYR; the initial KH₂PO₄ concentration = 3 mmol/L; adsorbent dose = 2 g/L; and agitation temperature = 25 °C)

3 Results and discussion

3.1 Weight ratio of K₂CO₃ to PYR

The weight ratio of K₂CO₃ to PYROMEX (PYR) was changed in the range of 1–5. Figure 1 shows the results of

equilibrium adsorption amounts for 10 samples; K(x) and K(x)-Δ, where x is 1–5. In Fig. 1, K(1–5) had similar Q_e value around 0.1 mmol/g, whereas K(3)-Δ reached 0.23 mmol/g and was better than K(1, 2, 4, and 5)-Δ. These results suggest that (1) the optimum amount of K₂CO₃ was 3 times greater weight than PYR, and (2) the heat treatment at 950 °C improved the phosphate adsorption of activated carbon fiber by 25–90%.

The heat treatment was done for the purpose of yielding quaternized nitrogen (N-Q) from other nitrogen species which would be the adsorption site for phosphate. The data of XPS analysis (N1s spectra) and the CHN elemental composition were shown in Table 1. The N-Q species was increased from 0.33 wt% (K(3)) to 0.46 wt% (K(3)-Δ) owing to the 950 °C heat treatment. This was one of the reason why K(3)-Δ was better adsorbent among the samples. K(1)-Δ contained high amount of not only N-Q but also N-X compared to K(3)-Δ. N-X contains N⁺–O[–] which would prevent phosphate from approaching to adsorbent surface. K(5)-Δ contained the lowest amount of N-Q and N among the heat-treated samples. The increase in the weight ratio of K₂CO₃ caused the decrease in N content. It means that the adsorption amount would be K(5)-Δ < K(3)-Δ < K(1)-Δ. However, the Q_e was not in proportion to N content.

Table 2 shows the specific surface area and pore structure of the samples. The S_{BET} of K(1) was the highest (2043 m²/g), because the pore structure was developed better than K(3) and K(5). In contrast, after heat treatment at 950 °C, K(5)-Δ showed the highest S_{BET} and pore volume. K(1)-Δ lost its surface area to less than 1000 m²/g and

Table 1 The characteristics of activated carbons

Sample	XPS analysis (wt%)				Elemental analysis (wt%)			
	N-6	N-5	N-Q	N-X	C	H	N	O ^a
K(1)	–	–	–	–	74.8	0.5	6.7	18.0
K(3)	0.14	0.49	0.33	0.11	89.4	<0.1	0.9	9.6
K(5)	–	–	–	–	89.1	<0.1	0.6	10.2
K(1)-Δ	0.19	0.19	0.50	0.30	87.9	<0.1	1.3	10.7
K(3)-Δ	0.30	0.40	0.46	0.19	90.0	<0.1	1.2	8.7
K(5)-Δ	0.05	0.24	0.25	0.20	85.6	<0.1	0.5	13.8

^aBy balance

Table 2 The specific surface area and pore structures of activated carbons

Sample	S _{BET} (m ² /g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)	V _{meso} ^a (cm ³ /g)	D _{avg} (nm)
K(1)	2043	0.998	0.991	0.007	1.95
K(3)	1723	0.807	0.801	0.007	1.87
K(5)	1800	0.675	0.669	0.006	1.82
K(1)-Δ	874	0.411	0.407	0.004	1.88
K(3)-Δ	1277	0.559	0.553	0.006	1.75
K(5)-Δ	1943	0.911	0.905	0.007	1.92

^aBy balance

Fig. 2 The phosphate adsorption isotherm of K(3)-Δ and K(3) (the initial KH_2PO_4 concentration = 0.1–30 mmol/L; adsorbent dose = 2 g/L; contact time = 24 h; and agitation temperature = 25 °C)

could not improve the adsorption capacity, while K(3)-Δ increased the Q_e from K(3), which was as much phosphate adsorption amount as K(1). Furthermore, the results shown in Tables 1 and 2 would suggest that although K(1) was activated well leading to the largest specific surface area, the carbon structure was not strict enough causing the large decrease in S_{BET} , V_{total} , V_{micro} , V_{meso} , and N content through the 950 °C heat treatment. On the other hand, K(3) and K(5) were damaged mildly and preserved their S_{BET} and N content.

According to these results, (1) the amount of N-Q and (2) the specific surface area were essential for phosphate adsorption. However, these points could not explain the reason why K(3)-Δ was better adsorbent than K(3). K(3) was better than K(3)-Δ from the viewpoints of S_{BET} , pore volume, and the ratio of N-Q to N-X, which were 3 for K(3) and 2.4 for K(3)-Δ, while the calculated N-Q amount on a unit area was 0.008 and 0.015 (mol/6.022 × 10²³ nm²) in K(3) and K(3)-Δ, respectively. The number of N-Q per 1 nm² could lead to the increase in Q_e of K(3)-Δ compared to K(3).

3.2 Adsorption isotherms and kinetics

The Langmuir adsorption isotherm curves were illustrated in Fig. 2 and their parameters were tabulated in Table 3. The maximum adsorption capacity (Q_m) of phosphate by K(3)-Δ reached 0.68 mmol/g and the value of the equilibrium adsorption affinity (K_e) was 0.32 L/mmol (Table 3). Meanwhile, K(3) showed very low Q_m (0.16 mmol/g) but its K_e (1.37 L/mmol) was higher than K(3)-Δ because K(3) shown higher S_{BET} and pore volume. Apparently, the 950 °C heat treatment was quite efficient to improve the phosphate adsorption capacity for K(3) due to increase the amount of adsorption sites, whereas it slightly decreased the surface structure and K_e . The maximum adsorption capacity for various adsorbents was summarized in Table 4. Among adsorbents including activated carbon, K(3)-Δ had a great adsorption ability.

The results of adsorption kinetics were shown in Fig. 3, and the parameters of pseudo-first- and second-order

Table 3 The parameters of adsorption isotherm and pseudo-first- and second-order model for kinetics

Sample	Adsorption isotherm			Kinetics				
	Q_m (mmol/g)	K_e (L/mmol)	R^2	Pseudo-first-order		Pseudo-second-order		
				k_1 (/h)	R_1^2	k_2 (/h)	Q_{e2} (mmol/g)	R_2^2
K(3)	0.16	1.37	0.908	1.21	0.462	97.3	0.11	0.993
K(3)-Δ	0.68	0.32	0.924	3.42	0.455	68.6	0.22	0.998

Table 4 Phosphate adsorption by some other adsorbents

Adsorbents	Chemical	Conditions	Q_m (mmol/g)	References
Fe–CaCl ₂ PVA	CaCl ₂	pH 7	0.61	[19]
Fe–MgCl ₂ PVA	MgCl ₂	pH 7	0.35	[19]
Fe–Mn oxide	FeSO ₄	25 °C, pH 7	0.17	[20]
Zeolite	LaCl ₃	20 °C	0.64	[22]
Al-biochar	AlCl ₃	pH 6	0.50	[23]
Prosopis juliflora-based AC	H ₂ SO ₄	30 °C, pH 6.7	0.14	[24]
Fe-AC (commercial)	–	22 °C, pH 6.5	0.11	[25]
Lanthanum-ACF (commercial)	La(NO ₃) ₃	10 °C	0.08	[26]
PAN-based ACF	steam	25 °C	0.22	[35]
PAN-based ACF	K ₂ CO ₃	25 °C	0.68	This study

Fig. 3 The phosphate adsorption rate onto K(3) and K(3)-Δ (the initial KH_2PO_4 concentration = 3 mmol/L; adsorbent dose = 2 g/L; and agitation temperature = 25 °C)

were presented in Table 3. The adsorption curve in Fig. 3 was calculated and illustrated using pseudo-second-order model (k_2 and Q_{e2}) [43]. As can be seen in Fig. 3, the phosphate adsorption for both K(3) and K(3)-Δ reached 90% of its adsorption amount (Q_e) within 15 min and equilibrium within 1 h. Based on their coefficient value, pseudo-second-order model was well fitted to both adsorbents.

3.3 Effect of pH on phosphate adsorption

The plots of equilibrium pH (pH_e) and Q_e were shown in Fig. 4. In order to adjust the solution pH, 1 mol/L HCl or NaOH was used. Various initial pH ($1 < \text{pH}_0 < 11$) greatly affected the adsorption capacities. Generally, phosphate adsorption reaches maximum amount under acidic condition, whereas basic condition causes low removal ability due to increasing OH^- [44]. Moreover, the dominant phosphate ion species are governed by the solution pH. Figure 4 showed that H_2PO_4^- was preferable species for N-Q under $2 < \text{pH} < 7$ rather than H_3PO_4 , HPO_4^{2-} , and PO_4^{3-} . The Q_e of K(3) and K(3)-Δ was increased to 0.12 and 0.23 mmol/g, respectively, with increasing pH up to 5–6. In the pH 6–8, K(3)-Δ remained its adsorption amount around 0.2 mmol/g, though the Q_e of K(3) and K(3)-Δ decreased at pH of higher than 6 and 8, respectively. Larger amount of hydroxyl ion would also prevent phosphate ion from adsorption onto N-Q site. Additionally, the surface of activated carbon fiber would be negatively charged at higher than pH of point zero charge (pH_{pzc}). In this study, the pH_{pzc} of K(3) and K(3)-Δ was obtained from the plots of pH_0 versus pH_e [45], and they were about 6.5 and 8.0,

Fig. 4 The effect of pH on phosphate adsorption for K(3) and K(3)-Δ, and phosphate species (the initial KH_2PO_4 concentration = 3 mmol/L; adsorbent dose = 2 g/L; and agitation temperature = 25 °C)

respectively. These results might indicate that phosphate adsorption onto N-Q of activated carbon fiber was improved in the pH range between 5 and 8, and inhibited under basic conditions.

3.4 Desorption

The calculated adsorption amount ratio ($Q_{e,2\text{nd}}/Q_{e,1\text{st}}$ [%]) was shown in Fig. 5 to examine the desorption ability of K(3)-Δ. In Fig. 5, HCl (3rd, 1 M) imitates to the Q_e proportion of third adsorption amount to first one ($Q_{e,3\text{rd}}/Q_{e,1\text{st}}$ [%]) and the Δ is the heat desorption method. Among the desorption methods using chemicals, the desorption with HCl was better efficient than that with NaCl and NaOH. This result suggested that regeneration under acid condition and exchanging H_2PO_4^- to Cl^- easily compared to OH^- were advantageous for K(3)-Δ. The HCl concentration for desorption also influenced the second cycle adsorption amount. It could be inferred that lower Cl^- concentration and stronger acid condition caused poor desorption ability (< 40%). On the other hand, the K(3)-Δ could adsorb phosphate by about 80% of its first adsorption amount after desorption with 1 mol/L HCl solution, and it could adsorb 60% at the third adsorption experiment. The desorption amount by heating at 950 °C would mean the maximum desorption ability because the ion binding between phosphate and N-Q would be decomposed absolutely during 950 °C heat treatment, and re-adsorption reached over 80%. The reason why

Fig. 5 The desorption experiments for K(3)-Δ (1st adsorption=100%, the initial KH_2PO_4 concentration=3 mmol/L; adsorbent dose=2 g/L; and agitation temperature=25 °C)

K(3)-Δ lost 20% adsorption amount would be a little decrease in N content and N-Q. Compared to this result, 1 mol/L HCl could be supposed to desorb phosphate ion almost completely. For the regeneration of K(3)-Δ, 1 mol/L HCl was better solution to desorb phosphate.

4 Conclusions

K_2CO_3 activation was effective for PYR, and the weight ratio of K_2CO_3 /PYR for the activation was related to specific surface area. The highest adsorption amount of 0.23 mmol/g was achieved for K(3)-Δ, which was activated at the weight ratio of 3 to PYR and then heated at 950 °C for 30 min. The phosphate adsorption would depend on three parameters; specific surface area (m^2/g), nitrogen content (wt%), and the number of N-Q on a unit area ($\text{mol}/6.022 \times 10^{23} \text{ nm}^2$). K(3)-Δ exhibited relatively high phosphate adsorption capacity (0.68 mmol/g) and rapid adsorption rate to reach equilibrium (< 1 h) as well. Furthermore, HCl acid was effective regeneration agent to desorb phosphate from K(3)-Δ.

Acknowledgements We thank Prof. Dr. Fumio Imazeki, the head of Safety and Health Organization, Chiba University, for the financial support on our study.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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