



A weak-base fibrous anion exchanger effective for rapid phosphate removal from water

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ABSTRACT

This work investigated that weak-base anion exchange fibers named FVA-c and FVA-f were selectively and rapidly taken up phosphate from water. The chemical structure of both FVA-c and FVA-f was the same; i.e., poly(vinylamine) chains grafted onto polyethylene coated polypropylene fibers. Batch study using FVA-c clarified that this preferred phosphate to chloride, nitrate and sulfate in neutral pH region and an equilibrium capacity of FVA-c for phosphate was from 2.45 to 6.87 mmol/g. Column study using FVA-f made it clear that breakthrough capacities of FVA-f were not strongly affected by flow rates from 150 to 2000 h⁻¹ as well as phosphate feed concentration from 0.072 to 1.6 mM. Under these conditions, breakthrough capacities were from 0.84 to 1.43 mmol/g indicating high kinetic performances. Trace concentration of phosphate was also removed from feeds containing 0.021 and 0.035 mM of phosphate at high feed flow rate of 2500 h⁻¹, breakthrough capacities were 0.676 and 0.741 mmol/g, respectively. The column study also clarified that chloride and sulfate did not strongly interfere with phosphate uptake even in their presence of equimolar and fivefold molar levels. Adsorbed phosphate on FVA-f was quantitatively eluted with 1 M HCl acid and regenerated into hydrochloride form simultaneously for next phosphate adsorption operation. Therefore, FVA-f is able to use long time even under rigorous chemical treatment of multiple regeneration/reuse cycles without any noticeable deterioration.

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1. Introduction

Discharging of concentrated phosphate into the water will cause serious adverse effects to natural aquatic ecosystems and severely deteriorates the water quality [1]. When high phosphate concentrations persist in water, algae and other aquatic plant life will flourish eventually causing decreased dissolved oxygen levels and eliminating photosynthesis and productivity in the water [2]. Moreover, algal blooms lead the foul odors and bad flavor and toxic algae (red tide) kills the desirable fish because of oxygen depletion in water [2,3]. The growth of macrophytes and phytoplankton is stimulated principally by phosphorus and nitrogen. The growth of rooted aquatic macrophytes will interfere with navigation, aeration, and channel capacity as well the dead macrophytes and phytoplankton will cause of microbial breakdown processes [2,4]. Therefore, the trace amount of phosphate in lakes, bays, coastal areas, and inland seas is also liable for eutrophication. The low concentration of phos-

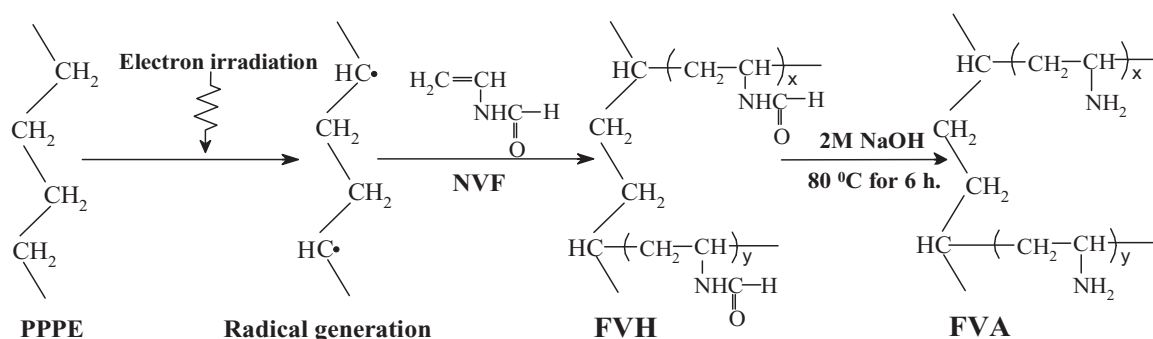
phate less than 1.0 mg/L caused the unexpected growth of algae in lakes and coastal bays [1,5,6]. For this reason, new mandate has been established for phosphorus reduction in wastewater effluent at 10 μg/L [7].

Many techniques have been proposed for phosphate removal from water and wastewater such as iron coagulation [8–10], biological removal [11–13] and adsorption by selective adsorbents [14–21]. A feasible method is necessary for removing phosphate from water to relieve the eutrophication. It is reported that precipitation and biological methods are not able to take up phosphorus completely or reduce its concentration near to zero or below 10 μg/L [12]. Several researchers also proposed ligand exchange adsorbents; these are cation exchange and chelating resins on which hard Lewis acid cations, such as Zr(IV), Fe(III), Al(III), and Mo(VI), are loaded [22–27]. Among these techniques, adsorption by selective adsorbents is promising and the most attractive and efficient methods for purification and separation of phosphate from water and wastewater [9,18]. Granular adsorbents and ligand exchange adsorbents, however, unable to take up anions especially phosphate efficiently in column adsorption at high feed flow rates more than 50 h⁻¹.

Most of the commercially available anion exchange resins based on crosslinked poly(styrene) matrices do not exhibit high

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Scheme 1. Synthetic route of the anion exchange fiber with primary amino groups.

selectivity to phosphate because of high hydrophobic nature of their polymer matrices and they prefer less hydrated anions to highly hydrated anions so long as anions have the same charge number [28]. Since no anion exchange resin having aliphatic crosslinked polymer matrices without any aromatic moieties has been commercialized yet, the selective removal of phosphate by commercialized resins is difficult to perform. Recently, we have reported a novel weak-base fibrous anion exchanger named FVA containing aliphatic crosslinked polymer matrices having primary amino group and shows hydrophilic characteristics [29]. This FVA is a rare organic anion exchanger, which prefers phosphate in the presence of competing anions such as chloride, nitrate, perchlorate and/or sulfate [6,9,23]. In this work, we have studied equilibrium phosphate uptake with FVA as a function of equilibrium pH in the absence and presence of competing anions such as chloride, nitrate or sulfate by means of the batch approach. In addition, we have also studied the detail behavior of FVA in column adsorption under various conditions using the same FVA packed column to check the reproducibility and reusability from the stand point of long-term uses.

2. Materials and methods

2.1. Materials

All materials and chemicals were of analytical grade and used as purchased without further purification. Two types of FVA were used in this study. One was non-woven cloth type fiber named FVA-c and the other filamentary type fiber named FVA-f. The major steps for preparation of both FVA-c and FVA-f are shown in Scheme 1. Properties and additional information of FVA are available elsewhere [29]. Ultra-pure water prepared by a Milli-Q Academic-A10 (Nippon Millipore Co., Tokyo, Japan) was used throughout. Phosphoric acid (85 wt%) and Na₂H₂PO₄·12H₂O were guaranteed grade and were obtained from Wako Pure Chemical Industries Ltd., Osaka, Japan.

2.2. Batch study

FVA-c was used as free amine form. A series of 0.010 M phosphate solutions at different pH values were prepared by mixing of 0.010 M H₃PO₄ with 0.010 M Na₂HPO₄. Test solutions (50 mL) were taken into a series of Erlenmeyer flasks (100 mL), and then FVA-c in free amine form was added into the flasks. All flasks were shaken in a temperature-controlled water bath with a mechanical shaker at 30 °C for 24 h at a constant agitation speed of 85 rpm to achieve equilibrium phosphate uptake of FVA-c. The amount of phosphate uptake by FVA-c was calculated from the differences between the initial phosphate concentration added to the FVA-c and the final phosphate concentration of the supernatant using the following

equation:

$$Q_e = \frac{(C_0 - C_f)V}{m} \quad (1)$$

where Q_e is the equilibrium phosphate uptake (mmol/g), V is the solution volume (L), and m is the mass of fibrous adsorbent FVA-c (g), C_0 and C_f are the initial and equilibrium phosphate concentrations in the solution, respectively. The pH and phosphate concentration of each supernatant at the equilibrium were measured. Here, phosphorus (P) concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Determination of P will be described in detail in a later section.

2.3. Column study

FVA-f in free amine form (0.50 g in dry state) was placed in a polyethylene column (inner diameter 1.3 cm) and equilibrated for 24 h in water. In this stage, the wet fiber bed volume in the column was 2.40 mL, which was used as the reference volume to convert the flow rate in mL/h into the space velocity (SV) in h⁻¹ as well as volumes of supplied solutions or water to the column in mL into bed volumes (BV) in mL/mL-fiber. First, FVA-f in free amine form was converted into hydrochloride form (F-NH₃⁺Cl⁻) as follows: 1 M HCl (100 mL) was supplied to the column at a flow of 10 h⁻¹ and then the column was washed with water (100 mL) at a flow rate of 20 h⁻¹. Flow rates of all solutions and water were expressed by SV, which is designated by the ratio F/V_{bed} in h⁻¹. Here F is the flow rate of a solution or water in mL/h and V_{bed} is the reference volume of the fiber bed in mL. All solutions or water volumes supplied to the column in adsorption–elution–regeneration operations are expressed by BV, which is designated by the ratio, $V_{supplied}/V_{bed}$; here $V_{supplied}$ is the volume of a feed supplied to the column in mL. Feeds containing phosphate were prepared by dissolving NaH₂PO₄·2H₂O in water and their final pH was adjusted with dilute HCl or NaOH, when needed. Feeds containing phosphate were also supplied to the column at a given flow rate. Prior to the elution and regeneration operations, the column was washed with water (100 mL) at a flow rate of 20 h⁻¹, and the adsorbed phosphate on the column was eluted with 1 M HCl (100 mL) at a flow rate of 10 h⁻¹. During elution of adsorbed phosphate with 1 M HCl, the column was simultaneously regenerated into hydrochloride form. After elution of phosphate, the column was washed with water (100 mL) for the next adsorption operation. In this work, the breakthrough point was designated as the feed volume supplied to the column up to $C/C_0 = 0.01$. Here, C_0 and C represent concentrations of phosphate in feeds and column effluents, respectively. The breakthrough capacity of FVA-f for phosphate was designated as phosphate uptake in mmol/g-fiber up to the breakthrough point. All column effluents including washings were collected on a fraction collector and P concentration in each fraction was determined by ICP-AES.

Table 1
Phosphate uptake by FVA-f under different feed flow rates and feed concentrations in column adsorption.

Entry no.	Feed			Breakthrough point (BV)	Breakthrough capacity (mmol/g)	Phosphate adsorbed (mmol/g)	Phosphate eluted (mmol/g)	Recovery (%)
	Flow rate (h ⁻¹ in SV)	C ₀ of phosphate (mM)	Volume (BV)					
1	150	1.61	400	185	1.43	2.49	2.43	97.6
2	500	1.62	400	168	1.31	2.29	2.35	102
3	1000	1.62	400	150	1.17	2.19	2.18	99.5
4	2000	1.57	400	142	1.07	2.00	2.01	100
5	1000	0.796	833	287	1.10	2.36	2.38	101
6	1000	0.402	1667	542	1.04	2.27	2.31	102
7	1000	0.072	5208	2435	0.841	1.52	1.55	102
8	2500	0.035	8333	4370	0.741	1.26	1.27	101
9	2500	0.021	11,667	6870	0.676	1.06	1.05	99.1

Wet fibers bed: 2.4 mL, feed solution pH 7.00 ± 0.10.

Table 2
Phosphate uptake by FVA-f under different concentrations of competing anions.

Entry no.	Feed			Breakthrough point (BV)	Breakthrough capacity (mmol/g)	Phosphate adsorbed (mmol/g)	Phosphate eluted (mmol/g)	Recovery (%)
	C ₀ of phosphate (mM)	NaCl (mM)	Na ₂ SO ₄ (mM)					
6	0.402			542	1.04	2.27	2.31	102
10	0.401	0.4		510	0.982	2.23	2.19	98.2
11	0.403		0.4	439	0.849	1.69	1.70	101
12	0.397	2.0		460	0.876	2.11	2.10	99.5
13	0.402		2.0	255	0.492	1.35	1.28	94.8

Wet fibers bed: 2.4 mL, flow rate of feed: 1000 h⁻¹, feed solution pH 7.00 ± 0.07, volume of feed: 1667 BV.

Table 3
Competitive uptake of phosphate and arsenate by FVA-f from a feed containing both arsenate and phosphate at 0.33 mM of each.

Entry no.	Breakthrough point (BV)		Breakthrough capacity (mmol/g)		Total uptake (mmol/g)		Amount eluted (mmol/g)		Recovery (%)	
	Phosphate	Arsenate	Phosphate	Arsenate	Phosphate	Arsenate	Phosphate	Arsenate	Phosphate	Arsenate
14	380	315	0.599	0.496	1.18	0.903	1.20	0.888	102	98.3
15	388	318	0.612	0.500	1.20	0.937	1.29	0.942	107	100

Conditions for feed: supplied volume 833 BV, pH ca. 7.0, flow rate 150 h⁻¹.

2.4. Determination of phosphorus by means of ICP-AES

The ICP-AES instrument used was a CID Plasma Photoemission Spectrophotometer IRIS (Nippon Jarrell Ash Co., Kyoto, Japan). The phosphorus standard solutions for calibration were purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan. The P concentration was analyzed at a wavelength of 213.6 nm according to the calibration curve method. The instrument was calibrated using four standard solutions containing 0, 2.00, 6.00 and 12.0 mg of P/L (for batch study, column study of entry nos. 1–7 in Table 1, entry nos. 10–13 in Table 2 and entry nos. 14 and 15 in Table 3) and the correlation coefficient of calibration curve was higher than 0.9999. For the determination of trace concentration of P below 1 mg of P/L (entry nos. 8 and 9 in Table 1), the instrument was calibrated using standard solutions of 0, 0.50, 1.00 and 2.00 mg of P/L and the correlation coefficient of calibration curve was also higher than 0.9999. In addition, sample solutions having complicated matrices were not used and no significant interference of matrices was observed.

3. Results and discussion

3.1. Characterization of FVA

Weak-base primary amine group fiber was synthesized by means of radiation induced liquid phase graft polymerization tech-

nique [29]. FVA-c and FVA-f were obtained by hydrolysis of FVH-c (non-woven cloth) and FVH-f (filamentary), respectively. However, both FVH-c and FVH-f were prepared under the same grafting conditions and the degree of grafting [29] was 152% and 114%, respectively. Based on chemical structures of FVH and FVA, the contents of C, H and N were determined. From CHN analyses, the nitrogen content of FVH-c and FVH-f were 10.56 and 4.75 mmol/g, respectively. Whereas, the nitrogen content after hydrolysis that of FVA-c and FVA-f in free amine form were 10.32 and 7.29 mmol/g, respectively. The nitrogen content of FVA-f increased after hydrolysis reaction as expected. Fig. 1 shows the FT-IR spectra of the FVH and FVA fibers in the functionalization steps. In FT-IR spectra (Spectrum One FT-IR spectrophotometer, PerkinElmer Instruments Ltd., USA), both FVH-c and FVH-f were exhibited strong absorption bands of amide carbonyl groups ca. 1670 cm⁻¹ and after hydrolysis (FVA-c and FVA-f) no absorption bands was observed but amine deformation band exhibited ca. 1600 cm⁻¹. In addition, the diameter of non-woven cloth and filamentary fiber were 15 μm and 12 μm, respectively.

3.2. Batch adsorption

FVA-c was contacted with phosphate solutions prepared by mixing of 0.010M phosphoric acid with 0.010M disodium hydrogen phosphate at various pH values from 2.31 to 7.1. The adsorbent

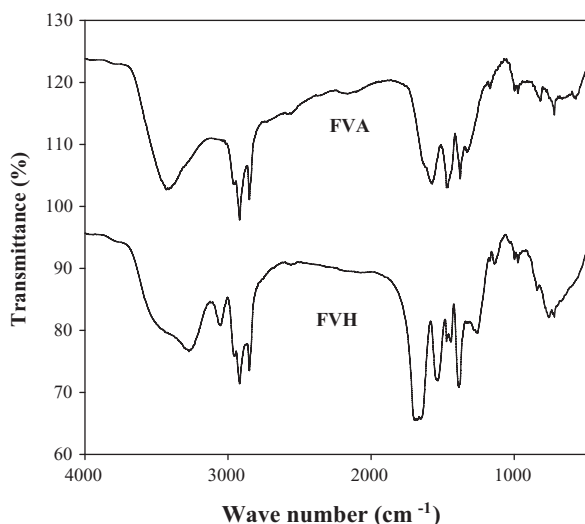


Fig. 1. Characterization of anion exchange fiber containing primary amine group by FT-IR spectra.

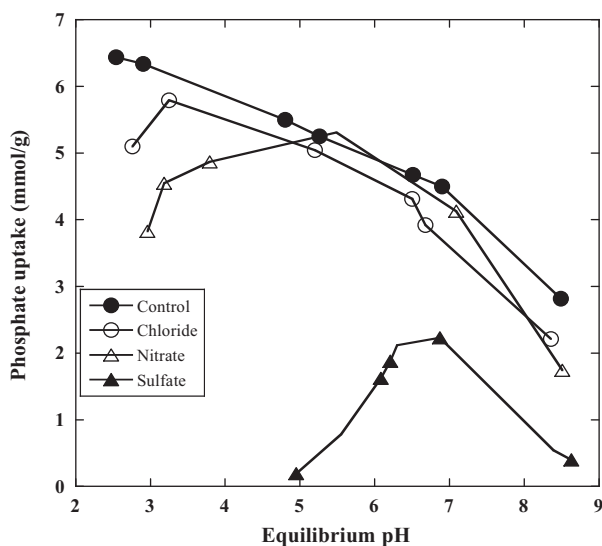
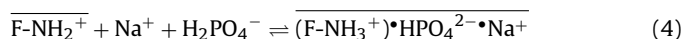
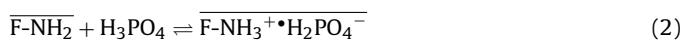


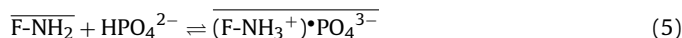
Fig. 2. Phosphate uptake as a function of equilibrium pH in the presence or absence of competing anions. Exchanger: FVA-c (50 mg in dry state); solutions: 0.010 M phosphate solution of various pH (50 mL) without and with a competing anion; equilibration: 30 °C for 24 h; competing anion concentration: 0.050 M of sodium salts of chloride, nitrate and sulfate.

(50 mg) was contacted with phosphate solution at 30 °C for 24 h in temperature-controlled water bath with a mechanical shaker. Fig. 2 shows dependence of phosphate uptake by FVA-c on equilibrium pH in the absence of competing anions. Here, initial pH of test solutions was 2.3–7.1. Phosphate uptake by FVA-c markedly decreased with an increase in pH. Because proton donating species in test solutions was H_3PO_4 or H_2PO_4^- and FVA-c was in the free amine form, equilibrium pH sharply increased from the initial pH as a result of phosphate uptake by FVA-c. For instance, when initial pH values were ca. 2.3 and 7.1, equilibrium pH values increased up to ca. 2.5 and 8.5, respectively. Therefore, phosphate uptake by FVA-c in the free amine form can be expressed by the following Eqs. (2)–(4):



The dissociation values of phosphoric acid as pK_{a1} , pK_{a2} and pK_{a3} are 2.16, 7.21, and 12.32, respectively [30], H_2PO_4^- and HPO_4^{2-} are taken up by protonated sites of FVA-c. In order to take up anions, F-NH_2 was protonated by accepting proton from H_3PO_4 and H_2PO_4^- species. Since dominant species is H_2PO_4^- in pH 4.6–7.2, sodium ion was taken up into the bulk of the fiber phase as shown in Eq. (4) above pH 4.6. Phosphate uptake by FVA-c decreased with an increase in pH; this can be ascribed to combined effects of a decrease in protonated sites and an increase in the fraction of HPO_4^{2-} species. It is well known that fraction of protonated sites of weak-base resins decreases with an increase in pH [31]. Below pH 4.6, however, anion exchange inactive species of H_3PO_4 increased with a decrease in pH, and in particular, H_3PO_4 becomes a primary species below pH 2.16 ($= \text{pK}_{a1}$). In addition, phosphate uptake is not only affected by pH but also affected by ionic strength and electrolyte concentrations [32]. However, phosphate solutions of different pH values were prepared by mixing of 0.010 M phosphoric acid with 0.010 M disodium hydrogen phosphate. Therefore, the ionic strength of the solutions was maintained constant during the batch study experimental work.

Chloride, nitrate and sulfate are main anionic species in rivers. Therefore, their effect on phosphate uptake was examined. Fig. 2 also shows uptake of phosphate as a function of equilibrium pH in the presence of chloride, nitrate and sulfate, respectively. The concentration ratio of phosphate and competing anions was 1:5. The chloride and nitrate little interfered with phosphate uptake by FVA-c. In presence of chloride, phosphate uptake by FVA-c at pH 8.4 was as high as 2.20 mmol/g, whereas in presence of nitrate, phosphate uptake by FVA-c at pH 8.5 was 1.8 mmol/g. As it is anticipated from Helfferich's electroselectivity, sulfate highly interferes with uptake of H_2PO_4^- by FVA-c; phosphate is not substantially taken up by FVA-c below pH 4.3, where main anionic species is H_2PO_4^- . The selectivity of ion exchangers is highly dependent by one counter ion in the presence of other counter ions. However, the valences of counter ions have strong effect on ion exchanger which may electrostatic (called electroselectivity) in the separation system [33–35]. According to the electroselectivity concept, ion exchangers generally prefer counter ions with higher valence to those with lower valence [31]. Then an electroselectivity principle is applicable for phosphate removal from water using ion exchange techniques in the presence of competing ions of chloride, bicarbonate, perchlorate, nitrate and/or sulfate [36]. Therefore, uptake of H_2PO_4^- by FVA-c was highly depressed by sulfate. With an increase in pH above pH 4.6, mole fraction of H_2PO_4^- decreases but that of HPO_4^{2-} increases, resulting in a decrease in the interference of sulfate. Phosphate uptake by FVA-c increased above pH 4.6 with an increased in pH up to pH 6.9 where the maximum uptake was 2.23 mmol/g observed. Many researchers have also been reported that higher pH (7.5–8.5) has positively affected of phosphate removal from water [32,37,38]. With a further increase in pH, phosphate uptake decreases. Above pH 7.21, primary species becomes HPO_4^{2-} , which cannot donate proton to free amine. In other words, the following reaction (5) did not take place because basicity of PO_4^{3-} was much higher than that of F-NH_2 :



Therefore, the amount of protonated sites decreases significantly with an increase in pH above 7.21, because mole fraction of HPO_4^{2-} attains unity at pH 9.76. Then, the maximum uptake was observed around pH 7. In the absence of a competing anion, phosphate uptake by FVA-c around pH 7 was 4.5–4.7 mmol/g and that in the presence of equimolar sulfate was 2.23 mmol/g. This means that FVA-c preferred HPO_4^{2-} to SO_4^{2-} . The higher selectivity of FVA-c to phosphate over sulfate comes from the fact that

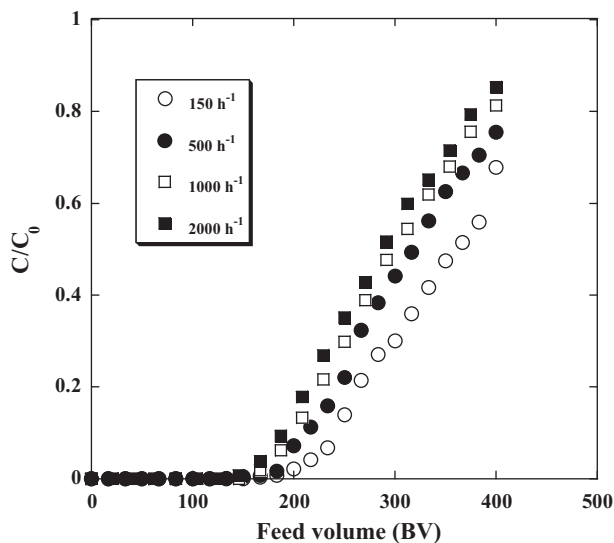


Fig. 3. Breakthrough profiles of phosphate uptake by FVA-f under different flow rates of feed in column adsorption. For detailed conditions and numerical results refer to entry nos. 1–4 in Table 1.

basicity of HPO_4^{2-} is much higher than that of Cl^- , NO_3^- or SO_4^{2-} and hydrogen bonding interaction is possible between F-NH_3^+ and HPO_4^{2-} [39,40].

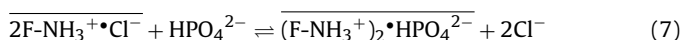
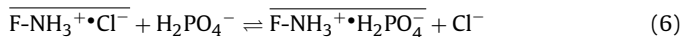
3.3. Column adsorption

3.3.1. Effect of feed flow rate

The outstanding characteristics of FVA are non-Hofmeister anion selectivity and rapid uptake of anionic species. Because the former is discussed in the preceding section, we would like to discuss kinetic aspects in phosphate uptake by FVA-f. First, therefore, the effect of flow rate of feed on phosphate uptake was examined in the feed flow rate range from 150 to 2000 h^{-1} using a 1.6 mM phosphate solution at pH ca. 7.0, while it seems that even the lowest flow rate of 150 h^{-1} in this work is higher compared with those for granular resin packed columns [22]. Since the breakthrough capacity is more important than the equilibrium capacity in the column adsorption of phosphate removal, the breakthrough capacity was evaluated in this work but not the equilibrium phosphate uptake capacity.

Fig. 3 shows breakthrough profiles of phosphate for four different flow rates of the feed. For detailed experimental conditions and numerical data, refer to entry nos. 1–4 in Table 1. Breakthrough points of phosphate slightly decreased with an increase in the flow rate of the feed. When the flow rate increased from 150 to 2000 h^{-1} , the breakthrough point decreased from 185 to 142 BV. This means that 13.3 times increase in flow rate brings only 22% decrease in the breakthrough point, indicating the high kinetic performances of FVA-f for phosphate uptake different from ligand exchange type adsorbents [22,24,25]. Indeed, the breakthrough capacity for phosphate by FVA-f was as high as 1.07 mmol/g even at the high flow rate of 2000 h^{-1} .

Since FVA-f in hydrochloride form was used in column uptake of phosphate, the following adsorption reactions occur:



In addition to conventional anion exchange mechanism, the hydrogen bonding interaction occurs in uptake of phosphate as described in the preceding section. Ligand exchange adsorbents are shown slow kinetics performances and unable take up selected

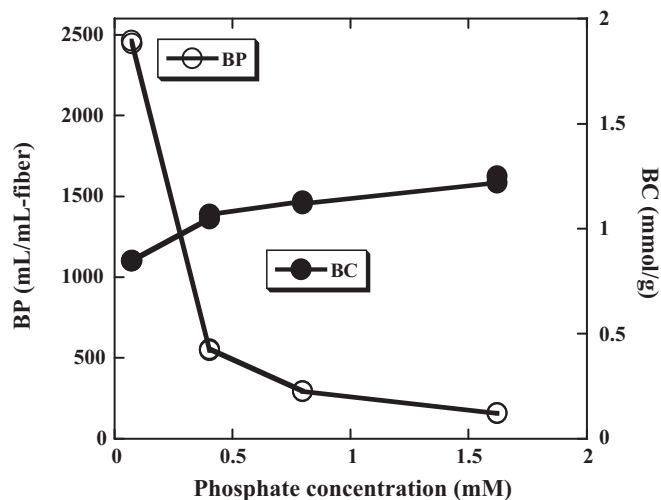


Fig. 4. Effect of initial phosphate concentration on phosphate uptake by FVA-f. For detailed conditions and results refer to entry nos. 3 and 5–7 in Table 1. BP and BC mean breakthrough point and breakthrough capacity, respectively.

anion species at high feed flow rate [41]. Therefore, anion exchange and hydrogen bonding interactions are much faster than ligand exchange adsorption reaction mechanism, in which ligands and/or solvent molecules initially coordinated to the central metal ion and then it is substituted by a target anion species [22,27]. Thus, FVA-f was effectively taken up phosphate in wide feed flow rate ranges from 150 to 2000 h^{-1} different from ligand exchange type adsorbents.

3.3.2. Effect of phosphate feed concentration

The phosphate removal by FVA is depended on buffering capacity of solution and that is the both functions of solution acidity and concentration of phosphate feed. Since breakthrough point is a dynamic quantity depending on not only flow rate of feeds but also concentration of a target ion, the effect of phosphate concentration in feeds (C_0) on breakthrough capacity for phosphate was examined using feed solutions containing phosphate from 0.072 to 1.62 mM at pH ca. 7.0. Here, the flow rate of feeds was fixed at 1000 h^{-1} . Results are given in Table 1 (entry nos. 3, 5–7) and Fig. 4, which shows breakthrough points and capacities as a function of feed solution concentration (C_0). With a decrease in feed solution concentration, the breakthrough point markedly increased but the breakthrough capacity decreased slightly. Fig. 4 clearly shows the decrease in the breakthrough capacity down to 0.40 mM in feed solution concentration was minor but became rather marked below 0.40 mM of C_0 . Since the breakthrough capacity is essentially equal to the product of the feed volume up to breakthrough point and feed solution concentration, it depends on the definition of the breakthrough point. For instance, the breakthrough point in this work was designated as the feed volume up to $C=0.01C_0$. Therefore, the lower the concentration of phosphate in the feed (C_0), an important the criterion for determining the breakthrough point, leading to the smaller breakthrough capacity. This probably is the reason for the breakthrough capacity profiles on phosphate feed concentration in Fig. 4. Indeed, 1% breakthrough capacities for phosphate uptake at feed concentrations of 0.79 and 0.40 mM were 1.10 and 1.04 mmol/g, respectively. Since phosphate concentrations in wastewaters are not so high in most cases [22] and it would be expected that FVA-f could be worked efficiently to remove phosphate from water with high breakthrough capacity as described in later section.

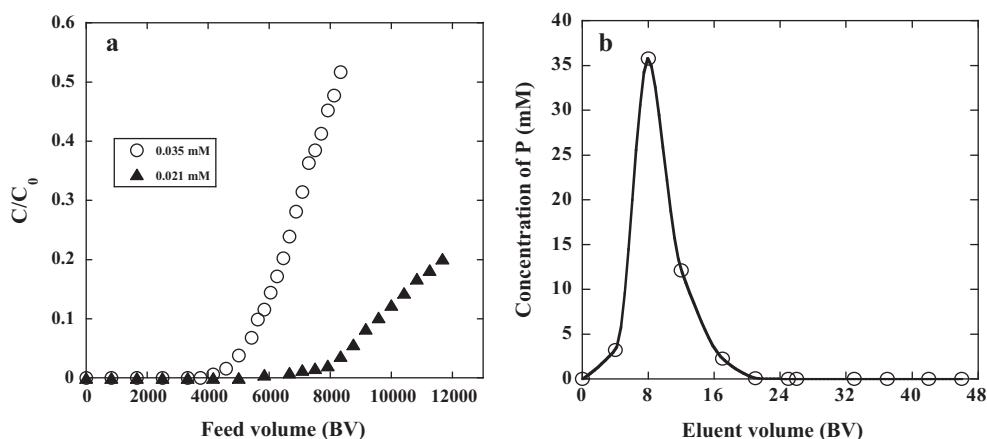


Fig. 5. (a) Phosphate uptake by FVA-f from feeds containing trace levels of phosphate at a feed flow rate of 2500 h^{-1} . For detailed conditions and numerical results refer to entry nos. 8 and 9 in Table 1. (b) Elution of adsorbed phosphate on FVA-f column with 1 M HCl at a flow rate of 10 h^{-1} . For detailed conditions and numerical data, refer to entry no. 9 in Table 1.

3.3.3. Rapid removal of trace phosphate

When huge volumes of water are contaminated with phosphate in mg/L levels, kinetically excellent adsorbents is very precious for rapid removal of phosphate under such conditions. Then, phosphate removal was tested by supplying two phosphate feeds containing 0.035 mM (3.33 mg/L of phosphate) and 0.021 mM (2.01 mg/L of phosphate) to the column at a flow rate of 2500 h^{-1} ; this corresponds to supply of 6.00 L phosphate feeds to a column having the fiber bed of 2.4 mL for 1 h. Fig. 5(a) shows breakthrough profiles of phosphate in these phosphate removal operations. The detailed experimental conditions and numerical results are given in Table 1 (entry nos. 8 and 9). In case of 0.035 mM of phosphate feed, the breakthrough point was 4370 BV and the breakthrough capacity was 0.74 mmol/g. In an alternative of 0.021 mM phosphate feed, the breakthrough point was 6870 BV and the breakthrough capacity was 0.67 mmol/g. This means that 16.5 L of water containing phosphate at 2.01 mg/L can be purified to less than $10 \mu\text{g/L}$ by 0.5 g packed FVA-f fiber, which is lower than the upper limit recommended by Florida Everglades Forever Act [7].

3.3.4. Regeneration and reuse

Since phosphoric acid is weak acid with $\text{pK}_{\text{a}1}$ value of 2.16, it substantially becomes non-charged species below pH 0.16. This means that adsorbed phosphate on FVA-f will be eluted by 1 M HCl according to the following reactions:

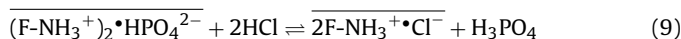
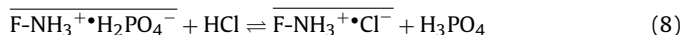


Fig. 5(b) illustratively shows the typical elution profile of phosphate in elution operation with 1 M HCl at a flow rate of 10 h^{-1} ; adsorbed phosphate on FVA-f packed column was quantitatively eluted with 20 BV of 1 M HCl as listed in Tables 1–3. From Eqs. (8) and (9), it is clear that this elution procedure simultaneously regenerate of FVA-f into hydrochloride form. After regeneration FVA-f in hydrochloride form, the column was rinsed with water to remove free hydrochloric acid for next adsorption of phosphate. Therefore, FVA-f was able to use to remove phosphate from water in many cycles. Similarly, the used of FVA-c in batch study, adsorbed phosphate was also eluted with 1 M HCl. The FVA-c was packed into the column and 1 M HCl (50 BV) was fed to the column at a flow rate of 10 h^{-1} to elute adsorbed phosphate and made the FVA-c in hydrochloride form. After removing excess hydrochloric acid with water, 1 M NaOH (40 BV) was feed to the column at 10 h^{-1} to change the FVA-c from hydrochloride form to free amine form. Finally, the

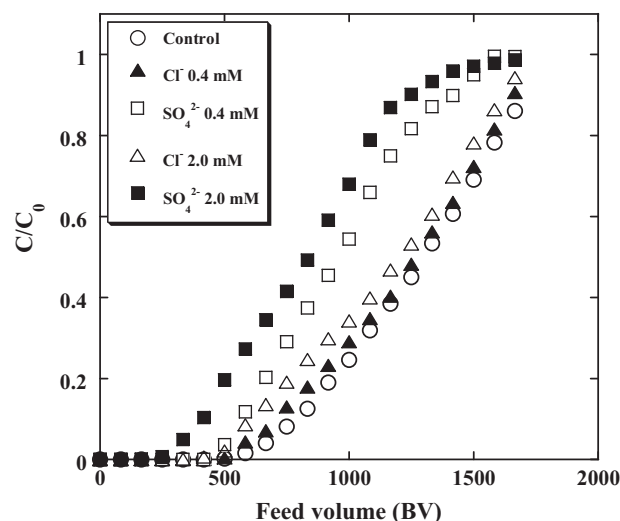


Fig. 6. Effect of competing anions on phosphate uptake by FVA-f. Detailed conditions and numerical results refer to entry no. 6, 10–13 in Table 2.

FVA-c was ready to use for next batch adsorption operation after rinsing with water to remove excess sodium hydroxide. Therefore, both FVA-c and FVA-f were able to use repeatedly.

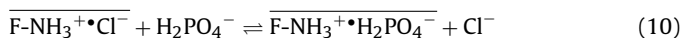
3.3.5. Effect of competing anions

Since main anions in river and lake waters are chloride and sulfate, their effect on phosphate uptake were tested using feeds containing chloride and sulfate as competing anions at equimolar or 5 times molar of phosphate in column approach. The concentration of chloride and sulfate in water is not so high but high concentration of chloride and sulfate are used to measure the selectivity and kinetic performances of FVA-f to phosphate. Fig. 6 shows the breakthrough curves of phosphate, and detailed experimental conditions and numerical results are summarized in Table 2. Phosphate uptake was not strongly affected in the presence of chloride; breakthrough capacities for phosphate in the presence of equimolar and 5 times molar chloride were 0.982 and 0.876 mmol/g, respectively. These values are comparable with the breakthrough capacity for phosphate (1.04 mmol/g) in the absence of competing anion under the same flow rate and feed solution concentration (entry no. 6 in Table 2). Total phosphate uptake was also not highly affected in the presence of chloride as listed in Table 2 (entry nos. 10 and 12); values of the total uptake were 2.23 and 2.11 mmol/g in the presence

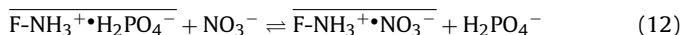
of equimolar and 5 times molar chloride, respectively. These values are close to total phosphate uptake in the absence of competing anions of 2.27 mmol/g (entry no. 6 in Table 2).

In the presence of equimolar sulfate, on the other hand, breakthrough capacity for phosphate (0.862 mmol/g) was not so markedly affected (entry no. 11 in Table 2) but the total uptake (1.70 mmol/g) was significantly less than the control one. In the presence of 5 times molar sulfate, interference by sulfate become more marked; breakthrough capacity for phosphate and total phosphate uptake decreased to 0.492 and 1.35 mmol/g, respectively (entry no. 13 in Table 2). However, these values are much greater than one-fifths of respective control values of 0.208 and 0.45 mmol/g, indicating that FVA-f prefer phosphate to sulfate, different from column study of phosphate uptake in the presence of sulfate by strong-base anion exchange resins [23,27]. In metal loaded ligand exchange type resins, phosphate uptake is not interfered with common anions but slightly enhanced the breakthrough capacity, but they are unable to take up phosphate effectively at high flow rates much higher than 100 h^{-1} [22].

In batch adsorption, FVA-c was used in free amine form and column adsorption, FVA-f was used in hydrochloride form. This study determined the selectivity as well as kinetic performances of FVA fiber towards phosphate over common competing anions. For instance, if the fiber (FVA-c) in chloride form was used for batch adsorption in the evaluation of effect of nitrate on phosphate, the number of counter ions becomes three (Cl^- , NO_3^- , and phosphate). Then, uptake of phosphate was affected by not only NO_3^- but also Cl^- . In other words, two ion exchange reactions (10) and (11) occurred simultaneously and this made it difficult to define and evaluate the effect of NO_3^- on phosphate uptake.



In case that the fiber (FVA-c) in free amine form was used, on the other hand, the number of counter ions becomes two. In this case, first H_3PO_4 and/or H_2PO_4^- change the fiber in free amine form into phosphate form, such as $\text{F-NH}_3^+\text{H}_2\text{PO}_4^-$ and $(\text{F-NH}_3^+)_2\text{HPO}_4^{2-}$. Then, the effect of NO_3^- was evaluated eliminating the effect of chloride as follows:



On the contrary to the batch study, the column adsorption was focused on removal of phosphate from dilute solutions of phosphate at neutral pH region. Under such conditions; the fiber in the hydrochloride form was used, because the low concentration of phosphate species was unable to change F-NH_2 into F-NH_3^+ . In addition, the batch adsorption clarified that chloride or nitrate did not strongly interfere with phosphate uptake. Therefore, FVA in free amine and hydrochloride form were used for batch and column adsorption, respectively.

3.3.6. Competitive uptake of phosphate and arsenate

Since phosphate is of concern in wastewater treatment and arsenic in drinking water treatment. Therefore, arsenic removal from water would always trump phosphate. However, chemistry of arsenic and phosphoric acids has very similar properties. We have reported that FVA-f has selectively taken up arsenate from water at high feed flow rate of 1000 h^{-1} [29]. Therefore, the competitive uptake of arsenate and phosphate by FVA-f was investigated. Then, the competitive uptake of arsenate and phosphate by FVA-f was evaluated by supplying a feed containing equimolar of both anions (0.33 mM of each) to the FVA-f packed column at a flow rate of 150 h^{-1} . As judged from data in Table 1, the highest breakthrough capacity was observed at the flow rate of 150 h^{-1} , this flow rate was selected to observe more clearly the

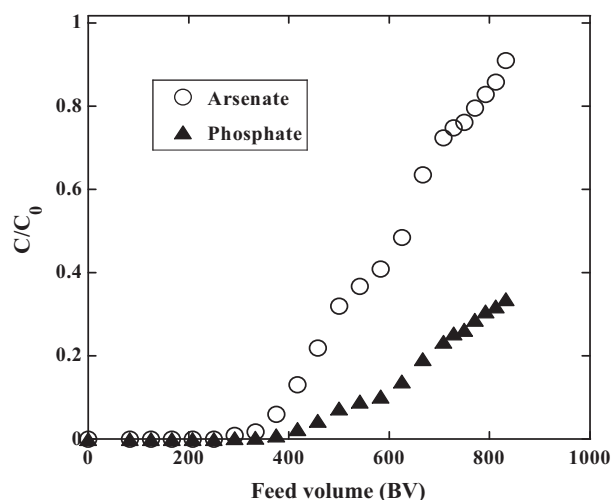


Fig. 7. Competitive uptake of arsenate and phosphate by FVA-f. Feed: a solution containing both arsenate and phosphate at 0.33 mM of each, pH 7.02, flow rate 150 h^{-1} . For detailed conditions and numerical results refer to Table 3.

difference in breakthrough capacities for both anions. Fig. 7 shows breakthrough profiles of both arsenate and phosphate. However, the detail conditions and numerical results are given in Table 3. The breakthrough point of arsenate (317 BV) was found to be smaller than that of phosphate (384 BV), leading to the breakthrough capacities of 0.498 and 0.606 mmol/g, respectively. After the breakthrough point of arsenate, the arsenate concentration in the effluent more sharply increased than that of phosphate. Therefore, total uptake of arsenate (0.920 mmol/g) was less than that of phosphate (1.19 mmol/g). These results reveal that FVA-f preferred phosphate to arsenate. Although both divalent arsenate and phosphate anions are able to form hydrogen bonding with F-NH_3^+ , the basicity of divalent arsenate is very similar to that of divalent phosphate since both parent acids have very close values of $\text{p}K_{a1}$, $\text{p}K_{a2}$, and $\text{p}K_{a3}$ [30]. Then, the significant difference does not exist in strength of the hydrogen bonding of each anion with F-NH_3^+ between HAsO_4^{2-} and HPO_4^{2-} species. On the other hand, meaningful difference can be seen between ionic sizes and charge density of both anions. In HAsO_4^{2-} , lengths of three equivalent As–O bonds are 0.1654–0.1671 nm and As–O bond length in As–OH is 0.1742 nm [42]. Similarly of HPO_4^{2-} , lengths of three equivalent P–O bonds are 0.1510–0.1524 nm and P–O bond length in P–OH is 0.1551–0.1564 nm [43]. On the other hand, the ionic radii of phosphate (0.17 Å) are also smaller than arsenate (0.335 Å) [44]. Therefore, crystallographic size or ionic radii of divalent phosphate anion is smaller than that of divalent arsenate anion and bear high charge density of divalent phosphate anion [45,46]. Then, it is estimated that Coulombic interaction between phosphate and positive sites is greater than that in case of arsenate, resulting in stronger interaction of phosphate with positive site than arsenate. Therefore, phosphate might overcome arsenate in competition for overall binding with positive sites.

It is very important to use the adsorbent without deterioration in its performances during many adsorption–elution–regeneration cycles for a long while. A major advantage of fibrous adsorbents is their retaining functionality and uptake capability in terms of adsorption activity after multiple regenerations cycles of adsorbent. However, the improvement of reproducibility of adsorbents remains a challenge; the weak-base fibrous adsorbent has capability for phosphate removal from water even after many cycles without any loss of original efficiency. All results in the column study were obtained using the same column without replacement of FVA-f for four months and each

adsorption–elution–regeneration operations were duplicated at least to check the reusability and reproducibility.

4. Conclusions

In this study, an extensive laboratory experimental work was carried out to determine the phosphate selectivity and kinetics performance by both batch and column study. In batch study, equilibrium phosphate uptake at pH 2.0–8.3 was as high as 6.87–2.45 mmol/g, respectively. FVA exhibits high selectivity to phosphate in the presence of competing anions such as chloride, nitrate and sulfate. Therefore, FVA exhibits non-Hofmeister anion selectivity sequence as phosphate > arsenate > chloride > nitrate > sulfate. Column study clarified that the protonated FVA-f was able to take up phosphate rapidly from the feed containing phosphate in different concentrations. The breakthrough capacities for phosphate were not strongly affected of feed flow rate from 150 to 2000 h⁻¹. Therefore, FVA-f showed high kinetic performances to take up phosphate at high feed flow rate. In competitive uptake of arsenate and phosphate by FVA-f, phosphate uptake was higher than arsenate uptake due to crystallographic size and charge density of phosphate for overall binding with positive sites of FVA-f. The adsorbed phosphate was quantitatively eluted with 1 M HCl and the FVA-f was regenerated simultaneously into hydrochloride form for the next adsorption operation after rinsing with water. Therefore, the fibrous anion exchanger was able to use repeatedly without any deterioration for long term to remove phosphate from water at high feed flow rate.

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