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Author(s)	Md. Rabiul Awal, M. A. Shenashen, Akinori Jyo, Hideaki Shiwaku, Tsuyoshi Yaita
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Preparing of novel fibrous ligand exchange adsorbent for rapid column–mode trace phosphate removal from water

Md. Rabiul Awual^{a,c*}, *M. A. Shenashen*^b, *Akinori Jyo*^c, *Hideaki Shiwaku*^a,
Tsuyoshi Yaita^a

^a *Actinide Coordination Chemistry Group, Quantum Beam Science Directorate, Japan Atomic Energy Agency (SPring-8), Hyogo 679-5148, Japan*

^b *Polymer Lab., Petrochemical Department, Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo, Egypt*

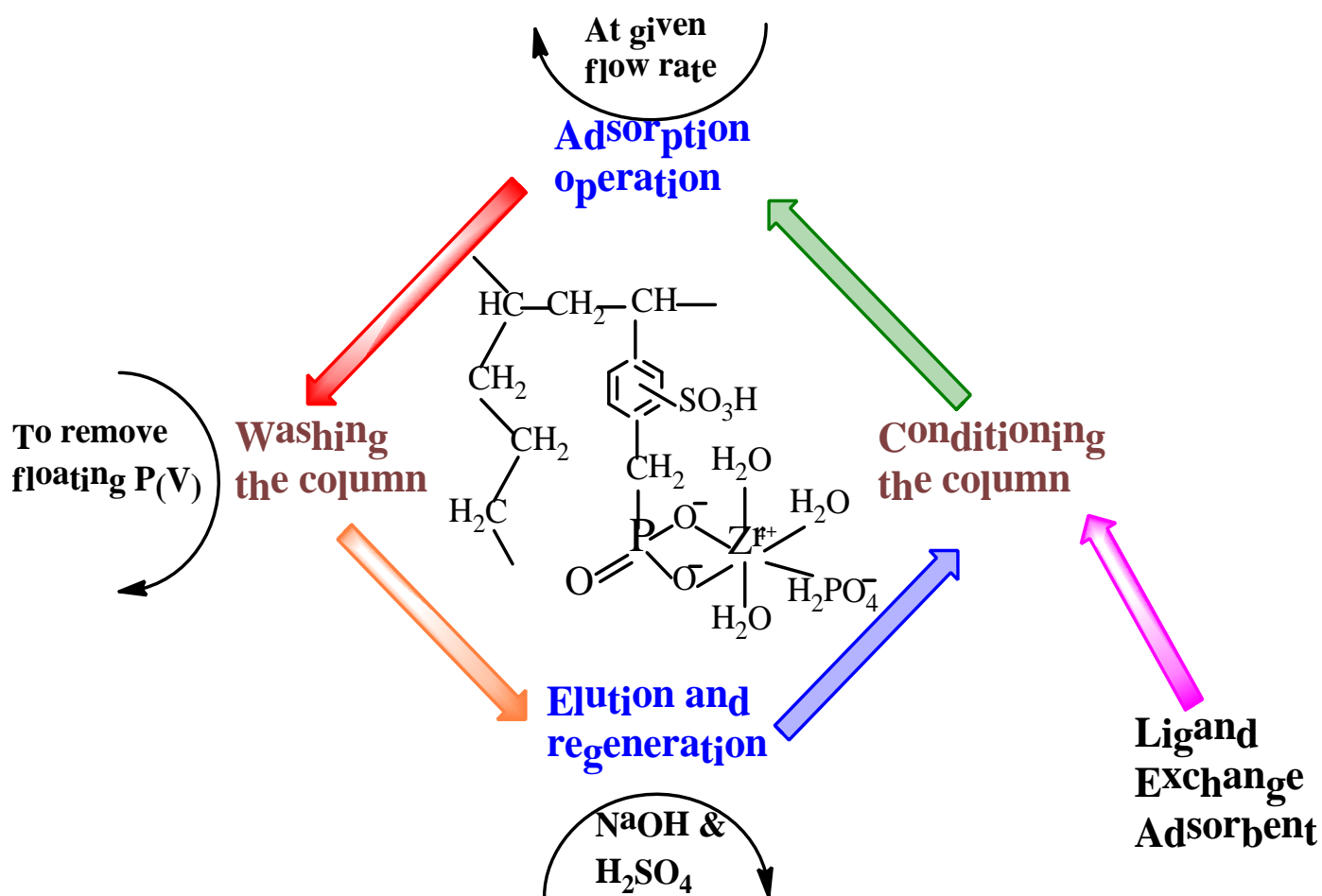
^c *Department of Applied Chemistry and Biochemistry, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan*

* Corresponding author. Tel.: +81-791-58-2642; fax: +81-791-58-0311.
E-mail address: awual.rabiul@jaea.go.jp, rawual76@yahoo.com (M. R. Awual).

Research highlights:

- Novel adsorbent is prepared and characterized for rapid trace phosphate removal.
- Trace phosphate can remove in the presence of competing ions at high flow rate.
- Phosphate can be removed without water pH adjustment with high efficiency.
- The adsorbent is reversible and reusable without deterioration in its performances.

Graphical Abstract



ABSTRACT

We developed a potentially high-performance adsorbent for sustainable treatment of soluble inorganic trace phosphate from water by zirconium(IV) loaded bifunctional fibers. In the presence of common Cl^- and SO_4^{2-} , phosphate adsorption was not adversely affected but slightly enhanced due to co-ion and Donnan invasion mechanism. Trace phosphorus (0.0143 mM) was also removed in presence of relatively high amounts of competing anions at high feed flow rate (850 h^{-1}). In competitive arsenate and phosphate adsorption, this novel adsorbent slightly preferred phosphate to arsenate. The adsorbent is reversible and keeps remaining functionality to further reuse in many cycles.

Keywords: Bifunctional fiber (FCPS); Ligand exchange adsorbent; Phosphate removal; High selectivity; Competitive adsorption.

1. Introduction

Eutrophication of water bodies such as rivers, lakes and inland seas is one of the most important environmental problems and phosphate is considered to be a key factor leading to this problem [1–3]. Consequently, phosphate removal from water bodies is an important issue to control eutrophication and conserve the natural aquatic environment. Therefore, recommended maximum permissible limit of phosphorus (P) in wastewater is 10–50 $\mu\text{g/L}$ to prevent such problem for living organisms [4]. On the other hand, phosphorous is a key nutrient element for living organisms but the excess amount adversely affected.

Many methods have been investigated for phosphate removal from wastewater namely physical and coagulation methods [5], chemical precipitation by using ferric, calcium or aluminium salts [6–8], biological removal [9], and adsorption [10–15]. However, physical methods are expensive and inefficient for phosphate removal from wastewater [5]. Chemical

precipitation and biological processes have been widely used but they suffered from high costs, sludge handling and operational difficulties with low efficiency for trace level of phosphate removal [16,17]. Many researchers have devoted their efforts in inventing new techniques to remove toxic anions and cations to ensure the safety of water for human consumption and to preserve the natural aquatic environment. Recently, ligand immobilized mesoporous adsorbent have attracted much attention for their accurate and rapid detection/removal/extraction of target ions [18–20]. Moreover, these are cost effective, easy to use, and show promise in capturing of metal ions. Adsorption is the most attractive technique based on economic and high efficiency approach for phosphate removal, particularly for low phosphate concentration in wastewater. Such features have shown intensive interest to many scientists as a suitable treatment technology [2,12,13,21]. Several types of phosphate adsorbents have been investigated such as natural and abundant wastes [10,11,14], primary amine containing fibrous anion exchangers [22,23], metals loaded ligand exchange chelating resins and fibers [17,24–26], aluminum/ferric oxide or hydroxide [27], fly ashes and activated carbon [28]. Many adsorbent have preferred to phosphate even in the presence of high concentration foreign anions but slow kinetics [13]. Several metals oxides adsorbents are unable to reuse and leaked the immobilized metal ion during phosphate adsorption or elution or regeneration operations [24,29].

In the case of metal loaded fibrous adsorbents, the metal ion is strongly retained on functional groups even for a large pH variation interval during adsorption and regeneration processes [17,30]. Moreover, these adsorbents have exhibited high kinetic performances with excellent high phosphate adsorption efficiency and capacity because the fibrous adsorbent possess short diffusion path and were able to remove phosphate at high feed flow rate [17]. In the monofunctional group such as phosphonic or phosphonate chelating resins/fibers, the metal ions immobilization is not high because of intraligand hydrogen bonding mechanism

[31] and this behavior causes relatively low removal efficiency of arsenate and phosphate from water [32]. Intraligand cooperation is playing an important role for enhancing metal–ion affinities to polymer matrix phase. Introducing a highly hydrophilic sulfonate group into the polymer matrix can eliminate intraligand hydrogen bonding [32]. Therefore, several resins and fibers have been prepared containing bifunctional groups based on specific preparation procedure and thermal stability [17,33,34]. In the present study, we have developed bifunctional cation exchange fibers having both phosphonate and sulfonate groups where the precursory fiber was grafted with chloromethylstyrene only for high immobilization of Zr(IV) onto fiber phase [33]. We have successfully immobilized the high amount of Zr(IV) immobilization for arsenate removal [30]. However, the present study is completely different based on fiber characterization and experimental conditions. The sulfonate group has enhanced the accessibility of metal ions into polymer matrix and consequently higher metal immobilization [17,24,32].

The bifunctional fiber has high affinity to hard Lewis acid cations such as Ti(IV), Fe(III) and Zr(IV). For example, Zr(IV) strongly binds to phosphonate group and make a very stable bond which remains in strong acid solution. It has been shown that Zr(IV) loaded bifunctional fiber can be efficiently used as a novel ligand exchanger for toxic anions removal from water [17,24]. Several researchers reported that Zr(IV) is ideal for ligand exchange adsorption for anions than Fe(III) [24,29]. The fixed–bed column adsorption processes are ideal candidates for reduction of dissolved phosphate to near–zero level and provide information on the long–term phosphate removal performance of the adsorbent. The main objectives of this study were following folds: (i) to investigate high immobilization of Zr(IV) onto fiber phase for developing novel adsorbent to remove phosphate with high adsorption efficiency and capacity, (ii) to study the high kinetic performances by dynamic flow tests of column packed fibrous adsorbent to investigate the effect of pH, selectivity to

phosphate over competing anions, initial concentration, feed flow rates, extremely high feed flow rate for trace phosphate removal, (iii) to evaluate competitive adsorption of arsenate and phosphate, (iv) to test the regeneration and the reuse of the synthesized adsorbent.

2. Materials and methods

2.1. Materials

All materials and chemicals were of analytical grade and used as purchased without further purification. Ultra-pure water prepared by a Milli-Q Academic-A10 (Nippon Millipore Co., Tokyo, Japan) was used throughout. $Zr(SO_4)_2 \cdot 4H_2O$, disodium hydrogenphosphate ($Na_2HPO_4 \cdot 2H_2O$) and disodium hydrogenarsenate ($Na_2HAsO_4 \cdot 7H_2O$) are guaranteed grade and were obtained from Wako Pure Chemical Industries Ltd., Osaka, Japan. Sulfuric acid, sodium hydroxide, nitric acid and perchloric acid were also purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan. Chloromethylstyrene was grafted onto polyethylene coated polypropylene precursory fiber by electron irradiation graft polymerization technique. The chloromethylstyrene was only grafted in this preparation from the stand point of high phosphorus content which may be suggested for high Zr(IV) immobilization and subsequently for high phosphate uptake. The major steps in the preparation of phosphonate and sulfonate group containing bifunctional cation exchange fiber (FCPS) are electron irradiation technique and followed by Arbusov reaction, chlorosulfonation and refluxed with concentrated hydrochloric acid as shown in **Scheme 1**. The used methods and properties of FCPS are reported elsewhere [33]. Phosphorus and sulfur contents were measured as reported method [17,30]. However, the acid capacity of FCPS in this study was 7.12 meq/g and its phosphorus and sulfur contents were 2.31 and 1.36 mmol/g, respectively. After grafting of chloromethylstyrene onto the precursory fiber, the degree of grafting of FCPS was evaluated to 147%.

2.2. Loading of Zr(IV) onto FCPS bifunctional fiber

Zr(IV) was immobilized onto FCPS in column approach. Dried FCPS (0.50 g) was packed into the polyethylene column (inner diameter 1.3 cm) and swollen for 24 h in water. Then, the fiber bed was carefully pressed with a glass rod with the flat ends until the height of the bed became constant. The volume of wet fiber bed in the column was 2.0 mL, which was used in the determination of space velocity (SV) and bed volumes (BV). The BV and SV were determined according to the reported method [30]. The Zr(IV) solution was prepared by dissolving $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in acidic media (0.5 M of H_2SO_4). An acidic 0.01 M Zr(IV) solution (100 mL) was fed into the column at a flow rate of 5 h^{-1} (mL/h/mL (adsorbent bed)). After washing the column with 0.5 M H_2SO_4 (30 mL) and water (30 mL), 0.2 M NaOH solution (30 mL) was fed into the column to check the stability of Zr(IV) onto FCPS. Several cycles of acidic and basic solvents solutions such as sulfuric acid and sodium hydroxide were fed to the column to check the stability and leakage of loaded Zr(IV) onto FCPS fiber. The total amount of immobilized Zr(IV) onto FCPS was calculated from the difference of Zr(IV) amounts contained into the fed solutions and the column effluent ones. After the column was washed with water and H_2SO_4 , acidic 0.01 M Zr(IV) solution (100 mL) was again fed into the column for more loading of Zr(IV) onto FCPS fiber. The loading operations of Zr(IV) onto FCPS were repeated six times. All column effluents were collected on a fraction collector and Zr(IV) concentrations in each fraction was measured by ICP–AES (IRIS, Nippon Jarrell Ash Co., Kyoto, Japan).

2.3. Phosphate adsorption and elution in column studies

Phosphate feed solutions were prepared by dissolving sodium dihydrogenphosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) in water and the pH of feed solutions was adjusted by dilute sulfuric acid

(0.01 M) and sodium hydroxide (0.1 M) solution, as needed. Similarly, arsenate feed solutions were also prepared by dissolving disodium hydrogenarsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) in water. Before adsorption operation, the column was conditioned at the same pH of the phosphate feed solutions. In case of neutral pH phosphate feed solutions, Zr-FCPS column was washed with water (60 mL) after elution and regeneration operations. Phosphate feed solutions were supplied to the column at designated feed flow rate. After each phosphates adsorption experiment, the column was rinsed with water (60 mL) at a flow rate of 10 h^{-1} . An elution operation was carried out by supplying of 0.2 M NaOH to the column at a flow rate of 5 h^{-1} . Then, the column was rinsed with water (60 mL) to be in neutral pH area. Finally, the Zr-FCPS column was regenerated with 0.5 M H_2SO_4 for the next phosphate adsorption experiment. All column effluents were collected on a fraction collector and zirconium, phosphorus and/or arsenic concentration in each fraction was determined by ICP-AES. The detailed procedures for phosphorus and arsenic determination by ICP-AES were reported elsewhere [12,22]. In addition, phosphorus was determined at 213.6 nm of emission intensities according to the calibration curve method by ICP-AES. In this work, the breakthrough point (beyond the feed concentration of 0.0323 mM of P) 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. In case of feed P concentration below 0.0323 mM, the breakthrough point was defined by the feed volume up to C of P = 0.01. The total phosphate uptake (TPU) by Zr-FCPS in adsorption operations was calculated from the following equation:

$$\text{TPU}(\text{mmol/g}) = (C_d V_d - \sum_{j=1}^n C_j V_j) / W \quad (1)$$

where C_d , V_d , and W are the concentrations of phosphorous in the feed, the volume of the

supplied feed, and amount of loaded dried bifunctional fiber, respectively. C_j and V_j are the phosphates concentration and the volume of the j -th fraction. The n is the number of the last fraction in the adsorption process. The breakthrough capacity is designated as phosphate adsorption in mmol/g-dry fiber up to the breakthrough point. Breakthrough capacity (BC) of phosphate by Zr-FCPS was calculated from the following relation:

$$BC(\text{mmol/g}) = (C_d V_p - \sum_{i=1}^{n_1} C_i V_i) / W \quad (2)$$

Here, V_p is the volume of the feed up to the breakthrough point and n_1 is the number of the last fraction up to the breakthrough point. The total eluted phosphate amount (TEP) was calculated from Eq. (3).

$$TEP (\text{mmol/g}) = (1/W) \sum_{q=1}^{n_2} C_q V_q \quad (3)$$

Here, C_q , V_q and n_2 are the concentration of phosphate and volume of the q -th fraction, and number of the last fraction in the elution operation. Recovery in each cycle was calculated by the following equation:

$$\text{Recovery (\%)} = (m_e/m_a) \times 100 \quad (4)$$

Here, m_a and m_e are stand for total phosphate adsorbed and total phosphate eluted amount, respectively. Here, amounts of phosphate adsorbed (m_a) was calculated by subtracting the sum of amounts of phosphate in each fraction of breakthrough experiments from a total amount of the phosphate fed into the column. In such calculation of many fractions in adsorption and elution operations, an error came from dilution phosphate concentration in each fraction as well as summation. Therefore, the precisions of 10–20% were usually

accepted in typical journals about separation sciences and water treatments. All experimental results for the column study were obtained using the same column for four months without renewing of Zr-FCPS column or reloading of Zr(IV) onto FCPS. Each run of adsorption–elution–regeneration operation was repeated at least two times to check the reproducibility and average data are presented in **Table 1, 2 and 3**.

3. Results and discussion

3.1. Loading of Zr(IV) onto FCPS for preparation of ligand exchange adsorbent

Intraligand hydrogen bonding mechanism is playing an important role for metal–ion affinities onto fiber. In the bifunctional group fibers have high affinity to Zr(IV) because of introducing a highly hydrophilic sulfonate group. This phenomenon implies the dual mechanism of bifunctional fibers for recognition of ligand responsible mechanism and ligand responsible for an access mechanism [32]. The Zr(IV) was bonded with oxygen atoms of phosphonate so strongly that the Zr(IV) adsorbed on FCPS does not appreciably leak in several operations. Moreover, sulfonic acid groups completely dissociate even in strongly acidic solutions resulting in elongation of the grafted polymer chains because of electrostatic repulsion between negatively charged sulfonate groups in the bifunctional fibers. Then Hard Lewis acid cation of Zr(IV) was strongly immobilized onto bifunctional fibers in strongly acidic media [30] for an effective ligand exchanger of phosphate adsorption. The phosphonate and sulfonate containing fibers have high affinity to Zr(IV) and Zr(IV) was strongly fixed on the fiber phase both in strong acidic and basic media. The possible bonding mechanism of Zr(IV) onto FCPS is shown in **Scheme 2** (inside). The immobilized amount of Zr(IV) onto FCPS was 1.03 mmol/g in the first run, which was much lower than its cation exchange or acid capacity [17,24]. Since FCPS became electronically neutral in a sulfuric acid solution, the loaded Zr(IV) onto FCPS in first was lower than expected. The

immobilized Zr(IV) was strongly retained on the fiber phase and leakage amount was completely negligible. Moreover, the present bifunctional fibers acid capacity, phosphorus and sulfur contents were evaluated to 7.12 meq/g, 2.31 and 1.36 mmol/g, respectively were relatively higher than the reported bifunctional fibers (acid capacity, phosphorus and sulfur contents were 4.22 meq/g, 0.94 and 1.91 mmol/g, respectively) [17]. Moreover, the recent reported FCPS acid capacity, phosphorus and sulfur contents were 7.10 meq/g, 2.16 and 1.54 mmol/g, respectively [30]. The present FCPS has a high adsorption ability of phosphate/arsenate based on the characterization. In addition, Zr(IV) immobilization also restricts by Zr(IV) ion diffusion into the inner fiber phase of FCPS and more amounts of Zr(IV) immobilization was expected. Then Zr(IV) loading procedure was repeated six times and the amount of loaded Zr(IV) increased up to 1.82 mmol/g. Moreover, the Zr-FCPS column was treated with H₂SO₄ and NaOH solution to check the stability of immobilized Zr(IV) onto FCPS have shown that Zr(IV) was strongly retained onto FCPS and could behave as a good ligand exchanger for phosphate adsorption.

3.2. Effect of pH on phosphate adsorption

Generally, solution pH plays a significant impact on phosphate adsorption by ligand exchange adsorbent [17,35]. Phosphate species present in wastewater and seawater as H₃PO₄, H₂PO₄⁻, HPO₄²⁻ and PO₄³⁻ based on the pH area. The pK_{a1}, pK_{a2} and pK_{a3} for H₃PO₄ are 2.16, 7.21 and 12.32, respectively [36]. Therefore, the effect of pH on phosphate adsorption by Zr-FCPS was examined in the pH region between 2.03 and 9.51. These tests were carried out at constant experimental conditions with an initial solution concentration of 1.35 mg of P/L and feed flow rate at 100 h⁻¹. **Fig. 1** illustrated the effect of solution pH for phosphate removal by Zr-FCPS and numerical results and experimental conditions are summarized in **Table 1** (entry nos. 1–5). It is generally known that the negatively charged of monovalent and divalent

phosphate (H_2PO_4^- or HPO_4^{2-}) species are selectively trapped by ligand exchange or ion exchange reaction mechanism based on the acid dissociation constant values of phosphoric acid [12,17]. **Fig. 1** revealed that breakthrough points and total adsorptions were not sharply changed when the pH varied between 4.02 and 7.05. The breakthrough points decrease gradually with increasing pH from 2.03 to 4.02 (**Table 1**, entry nos. 1 and 2). However, the breakthrough points and total adsorption were significantly decreased (from 584 to 432 BV) with increasing pH from 4.02 to 9.51 as judged from **Fig. 1** and **Table 1** (entry nos. 2–5). The decrease in the phosphate ion adsorption implies a competition between phosphate ion and hydroxide for the adsorption by Zr–FCPS ligand adsorbent. Therefore, phosphate adsorption was decreased when Hard Lewis base or hydroxide increased in high pH area. This may be also possible in the combined with the pH of zero point charge (pH_{ZPC}). In fact, when the solutions pH values are lower than the pH_{ZPC} , the adsorbent was mainly positively charged and consequently retains huge amounts of negatively charged ions. When pH values are higher than the pH_{ZPC} , the adsorption of the negatively charged ions is very limited and decreased the phosphate adsorption capacity [10,37]. Moreover, pH of the natural water and municipal wastewater normally varies between 6.5 and 7.3 [38]. Therefore, H_2PO_4^- species will be the major phosphate species in the aqueous phase and under such conditions, the phosphate removal by ligand exchange adsorbent of Zr–FCPS will be favored. Indeed, the present study revealed that Zr–FCPS adsorbent was able to purify 541 BV of water containing 1.35 mg of P/L even at neutral pH area 7.05. However, acidic pH area is favourable for high breakthrough and total adsorption capacities as judged from pH 2.03 adsorption operation. Several researchers have also reported the same trend for metal ions loaded adsorbents to take up target ions [24,35]. Few adsorbents have high adsorption in neutral pH area such as metal oxide loaded polymeric ligand exchanger [25]. In practical viewpoint, pH-dependent adsorption is quite significant due to pH of the secondary

wastewater after biological treatment is usually neutral pH region and phosphate removal by Zr-FCPS adsorbent does not require any pH adjustment. Therefore, all other effects were carried out in neutral pH area in this work.

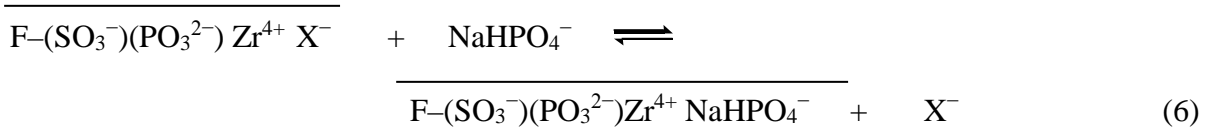
3.3. Effect of flow rate on phosphate adsorption

The lowest flow rate (100 h^{-1}) in this study is higher than the metal loaded resin ligand adsorbents [24]. In this study, the feed flow rate effect was evaluated from 100 to 500 h^{-1} when other experimental conditions were almost same. **Fig. 2** illustrated the phosphate adsorption by Zr-FCPS and experimental conditions and numerical results are summarized in **Table 1** (entry nos. 4, 6 and 7). The flow rate effect affected the residence time during the solution supplied to the column and treated in contact with the adsorbent. This causes affect the breakthrough and total adsorption capacity where the adsorption is diffusion controlled [39]. The flow rate in the columns was ranged from 100 to 500 h^{-1} and the corresponding operation times in the columns was from 600 to 120 min. Breakthrough and total adsorption capacities were sharply influenced by the flow rate as depicted in **Fig. 2** and **Table 1** (entry nos. 4 and 7). The breakthrough points decreased from 541 to 379 BV as flow rate was increased from 100 to 500 h^{-1} . This finding can be explained by the fact that lower is the flow rate, higher are the residence time, the breakthrough point and the adsorbed masses [40]. These adsorption capacities are comparable with other synthetic adsorbent even the Zr-FCPS was counted at breakthrough only [11]. On the other hand, Zr-FCPS ligand exchange adsorbent is working well to remove phosphate even at high feed flow rate compared with metal loaded granular resin packed columns where the optimal flow rate are at ca. 50 h^{-1} [12,26]. This is probably due to the fact that the fibrous adsorbents have short diffusion path leading to high kinetic performances than the granular resin adsorbents. However, the ligand

adsorbents are bit in slow kinetics than the weak–base type fibrous adsorbents due to anion exchange and hydrogen bonding reaction mechanisms by weak–base adsorbents [12].

3.4. Effect of competing anions on phosphate adsorption

Chloride and sulfate ions are commonly found in wastewater, and may interfere in the phosphate adsorption process by competing for the adsorption sites [10,14,25,38]. To assess the effect of these anions on phosphate adsorption, 0.0435 mM phosphate solution containing of 2.0 mM NaCl and Na₂SO₄ in each or together was used as feed solution. **Fig. 3** illustrated the breakthrough profiles of phosphate in an evaluation of competing anions effect. The experimental conditions and numerical results are summarized in **Table 2** (entry nos. 4 and 8–10). In the presence of 2.0 mM Cl[−], phosphate adsorption was not affected but the breakthrough point and total adsorption slightly increased ca. 7% as judged from **Table 2**, entry nos. 4 and 8. On the other hand, in the presence of 2.0 mM SO₄^{2−}, phosphate adsorption was also ca. 9% enhanced (entry nos. 4 and 9 in **Table 2**). However, the enhancement differences between SO₄^{2−} and Cl[−] were insignificant in this stage. Moreover, in the presence of both Cl[−] and SO₄^{2−}, breakthrough and total adsorption capacities (0.106 and 0.175 mmol/g, respectively) were higher than the control one (**Table 2**, entry nos 4 and 10). An enhancement of anion adsorption in the presence of such electrolyte has also been observed in some chelating adsorbents [17,24,26,35]. This behavior is probably due to the fact that the increase as the sodium ion concentration in the aqueous phase shifts the equilibrium toward the products and maintains electroneutrality through the Donnan invasion mechanism according to the following reactions [41]:



The ligand exchange adsorbents are not adversely affected for phosphate adsorption in presence of common anions because of the ion pair in inner sphere complex formation and co-ions effects [24,25]. On the contrary, polymeric adsorbents are adversely affected in phosphate adsorption due to outer-sphere complexes formation through electrostatic interaction, ion exchange and surface complexes, and the divalent anions are generally more preferred to be adsorbed than the monovalent anions according to the electroselectivity [22].

3.5. Rapid removal of trace phosphate

In wastewater, the phosphorus concentration is not high, whereas its co-existing anions are mainly chloride and sulfate [13,24]. Therefore, kinetically high adsorption rate adsorbent is required to remove low concentration phosphate even in the presence of high concentration of common anions. The aqueous solution containing phosphates, chlorides and sulfates with concentrations of 0.014, 2.0 and 2.0 mM respectively was fed to the column at a relatively high flow rate of 850 h⁻¹. **Fig. 4** shows the breakthrough profile of phosphate and experimental conditions and numerical results are summarized in **Table 2** (entry nos. 11 and 12). Changing the flow rate up to 850 h⁻¹, breakthrough and total adsorption capacities were affected compared with 500 h⁻¹ flow rate (**Table 1**, entry no. 7). In other words, the breakthrough point of phosphate adsorption at flow rate of 850 h⁻¹ was so much higher in 1109 BV, which corresponds to a breakthrough capacity of 0.063 mmol/g. This means that 2.22 L of water containing phosphorus at 0.0143 mM can be purified to less than 10 µg/L by Zr-FCPS fibrous adsorbent (0.50 g FCPS), which is lower than the permissible limit recommended by Florida Everglades Forever Act [4]. This finding revealed that Zr-FCPS fibrous adsorbent able to purify low concentration level of phosphate even in the presence of high concentration of common anions at high feed flow rate.

3.6. Elution, regeneration and reuses

When the adsorbent was saturated with phosphate species, simple tests were performed to see whether the adsorbent could be chemically eluted and regenerated. Hydroxide ion is the hardest Lewis base and can be used as effective eluent. Adsorbed phosphate on Zr-FCPS was eluted with 0.2 M NaOH at a flow rate of 5 h⁻¹. The eluent has quantitatively eluted the adsorbed phosphate from Zr-FCPS. **Fig. 5** shows an elution profile where phosphate was quantitatively eluted from Zr-FCPS column and sharp long tail peak were also observed due to strong binding between phosphate species and adsorbent. After the elution, the column was washed with water and then regenerated with 0.5 M H₂SO₄ solution at a flow rate of 5 h⁻¹. After regeneration operation, the column was again washed with water for next phosphate adsorption operation. The reuse cycle was possible as schematically illustrated in **Scheme 2**. During chemical treatment by NaOH and H₂SO₄ in elution and regeneration operations, no Zr(IV) was found in the column effluents. Therefore, Zr(IV) was retained onto FCPS strongly and Zr-FCPS can be used for the next adsorption–elution–regeneration without further Zr(IV) immobilization onto FCPS.

The preparation of FCPS required sophisticated instrument which is quite expensive. However, the high selectivity and sorption capacity including many cycles of operations without deterioration in its original performance, relatively high cost of FCPS will not a big barrier in practical application.

3.7. Competitive adsorption of phosphate and arsenate

Arsenate has a similar structure and deprotonation constants as phosphate in solution and these similarities between phosphate and arsenate complexes make it a possible competitive adsorption of both species. We have reported that weak–base amine type adsorbents and metal loaded ligand exchange adsorbents have selectively taken up arsenate

from water [27,30]. Then the competitive adsorption of arsenate and phosphate by Zr-FCPS was also performed for this study. Arsenate and phosphate adsorption by Zr-FCPS was evaluated by supplying a feed containing equimolar of both anions (0.0435 mM in each) to the column at a flow rate of 100 h^{-1} . Breakthrough profiles of arsenate and phosphate are illustrated in **Fig. 6** and the results and experimental conditions are summarized in **Table 3**. The breakthrough point of phosphate (337 BV) was higher than that of arsenate (285 BV) and the corresponding breakthrough capacity was 0.059 and 0.050 mmol/g, respectively (**Table 3**, entry no. 13). An effluent arsenate concentration was sharply increased after breakthrough points than that of phosphate (**Fig. 6**). Moreover, total phosphate adsorption (0.111 mmol/g) was also higher than that of arsenate (0.093 mmol/g). These results clarified that Zr-FCPS adsorbent was preferred to phosphate over arsenate in the competitive adsorption operations. This is probably due to the adsorbed ion was bound irreversibly, while the more slowly adsorbed ion was exchangeable with a competing ion introduced later. However, phosphate and arsenate adsorption at different electrolyte concentrations is not adequate to explain the real causes of competitive adsorption at this stage.

4. Conclusions

This study shows that zirconium(IV) loaded bifunctional cation exchange fibers can be considered tenable ligand exchange adsorbent for selective phosphate removal from aqueous solutions. The main parameter influencing the phosphate adsorption capacity by Zr-FCPS was the feed solution pH, feed flow rates, initial concentrations and trace phosphate concentration. Low pH was favorable for high adsorption but the neutral pH region also shown promising adsorption capacity. Phosphate adsorption was decreased by an increase of feed flow rates due to residence contact time. However, phosphate adsorption was not adversely affected in the presence of common ions because of co-ion and Donnan invasion

mechanisms. Trace level of phosphate was removed even at high feed flow rate of 850 h⁻¹. In competitive arsenate and phosphate adsorption, Zr-FCPS was preferred to phosphate than arsenate. The adsorbed phosphate on Zr-FCPS column was quantitatively eluted and regenerated for the next adsorption. No Zr(IV) was found in column effluents during many chemical treatments in adsorption–elution–regeneration cycles. Zr(IV) loaded bifunctional fibrous adsorbent is able to remove phosphate from wastewater efficiently to prevent eutrophication in the receiving water bodies for long time without any deterioration of Zr-FCPS functionality. Therefore, large scale pilot studies are recommended in order to confirm the promising results obtained at laboratory scale.

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Table 1

Phosphate adsorption by Zr-FCPS under different feed solutions pH and feed flow rates in column approach

Entry no.	Feed				Breakthrough point (BV)	BC (mmol/g)	TPU (mmol/g)	TEP (mmol/g)	Recovery (%)
	solution pH	flow rate h ⁻¹ in SV	C ₀ of P (mM)	Volume (BV)					
1	2.03	100	0.0436	1000	640	0.112	0.174	0.176	101
2	4.02	100	0.0435	1000	584	0.102	0.172	0.170	98.8
3	5.53	100	0.0438	1000	556	0.097	0.170	0.165	97.1
4	7.05	100	0.0435	1000	541	0.094	0.166	0.163	98.1
5	9.51	100	0.0435	1000	432	0.075	0.157	0.160	102
6	7.01	200	0.0436	1000	494	0.086	0.161	0.157	97.5
7	7.03	500	0.0436	1000	379	0.066	0.152	0.146	96.1

Wet fiber bed: 2.0 mL.

Table 2

Phosphate adsorption by Zr-FCPS in presence of high concentration common anions and high feed flow rate

Entry no.	Feed					Breakthrough point (BV)	BC (mmol/g)	TPU (mmol/g)	TEP (mmol/g)	Recovery (%)
	C ₀ of phosphate (mM)	Flow rate h ⁻¹ in SV	NaCl (mM)	Na ₂ SO ₄ (mM)	Volume (BV)					
4	0.0435	100	–	–	1000	541	0.094	0.166	0.163	98.1
8	0.0437	100	2.0	–	1000	576	0.101	0.171	0.170	99.4
9	0.0436	100	–	2.0	1000	588	0.103	0.173	0.171	98.8
10	0.0436	100	2.0	2.0	1000	608	0.106	0.175	0.177	101
11	0.014	850	2.0	2.0	2200	1109	0.063	0.118	0.120	101
12	0.014	850	2.0	2.0	2200	1116	0.064	0.116	0.118	102

Wet fibers bed: 2.0 mL, pH of feed solutions: 6.96 ± 0.10 .

Table 3

Competitive adsorption of phosphate and arsenate by Zr-FCPS from a feed containing both arsenate and phosphate at 0.0435 mM in each

Entry no.	Breakthrough point (BV)		BC (mmol/g)		Total adsorbed (mmol/g)		Total eluted (mmol/g)		Recovery (%)	
	Phosphate	Arsenate	Phosphate	Arsenate	Phosphate	Arsenate	Phosphate	Arsenate	Phosphate	Arsenate
13	337	285	0.059	0.050	0.111	0.093	0.112	0.095	101	102
14	345	296	0.060	0.051	0.113	0.095	0.111	0.094	98.2	98.9

Conditions for feed: supplied volume 675 BV, pH ca. 7.0, flow rate 100 h⁻¹.

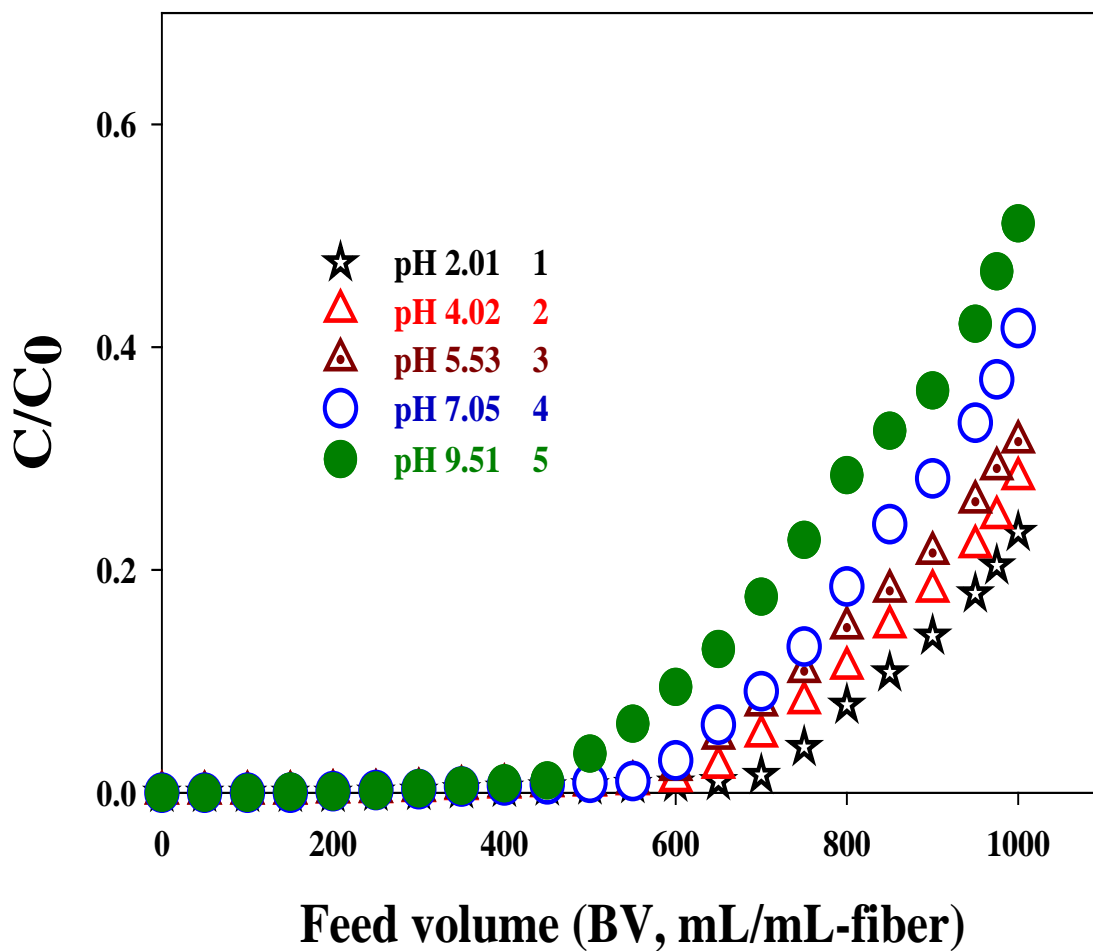


Fig. 1. Breakthrough profiles of phosphate adsorption by Zr-FCPS ligand exchange adsorbent under different feed solution acidity. Figure after pH values in the inset corresponds to entry nos. 1–5 in Table 1.

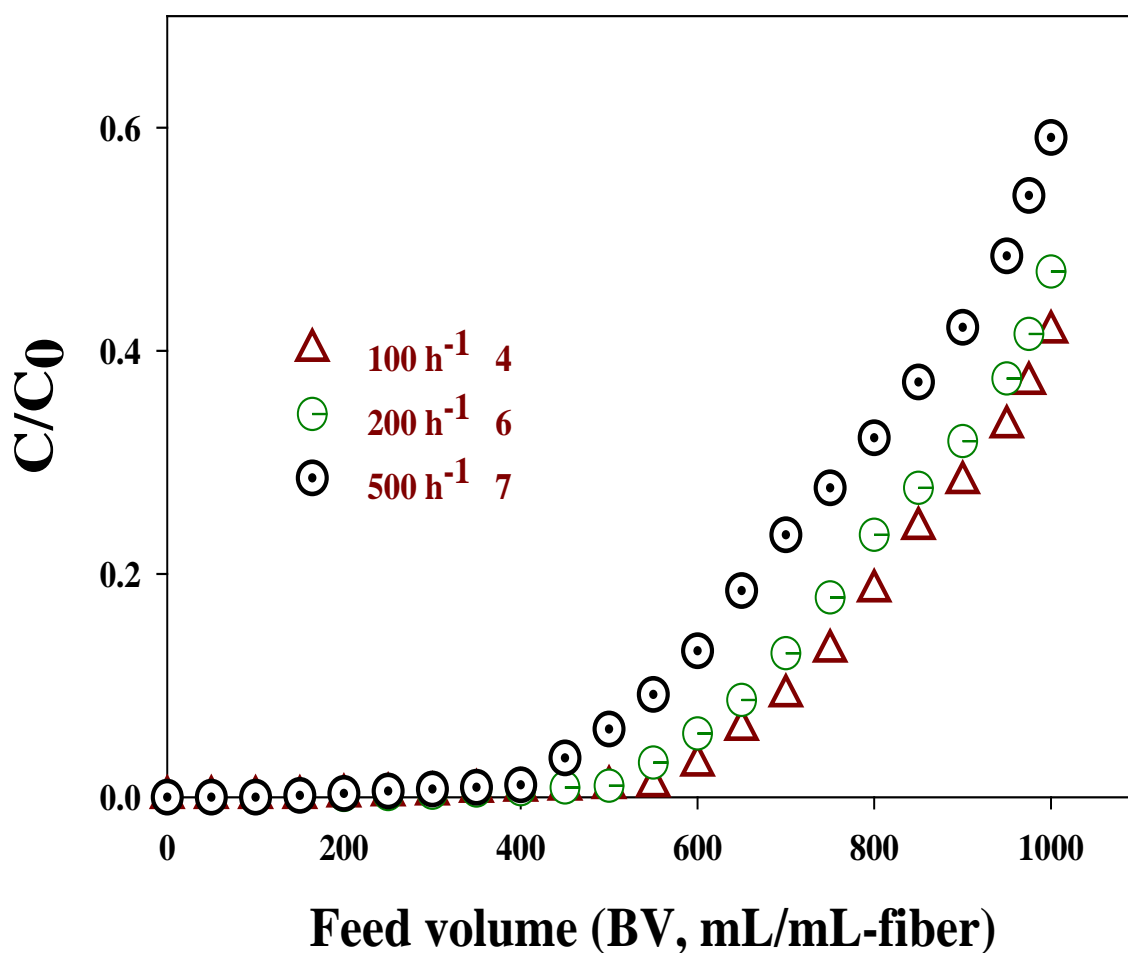


Fig. 2. Breakthrough profiles of phosphate adsorption by Zr-FCPS ligand exchange adsorbent in an influence of different feed flow rates. Figure after flow rate in the inset corresponds to entry nos. 4, 6 and 7 in Table 1. For detailed conditions and numerical results refer to entry nos. 4, 6 and 7 in Table 1.

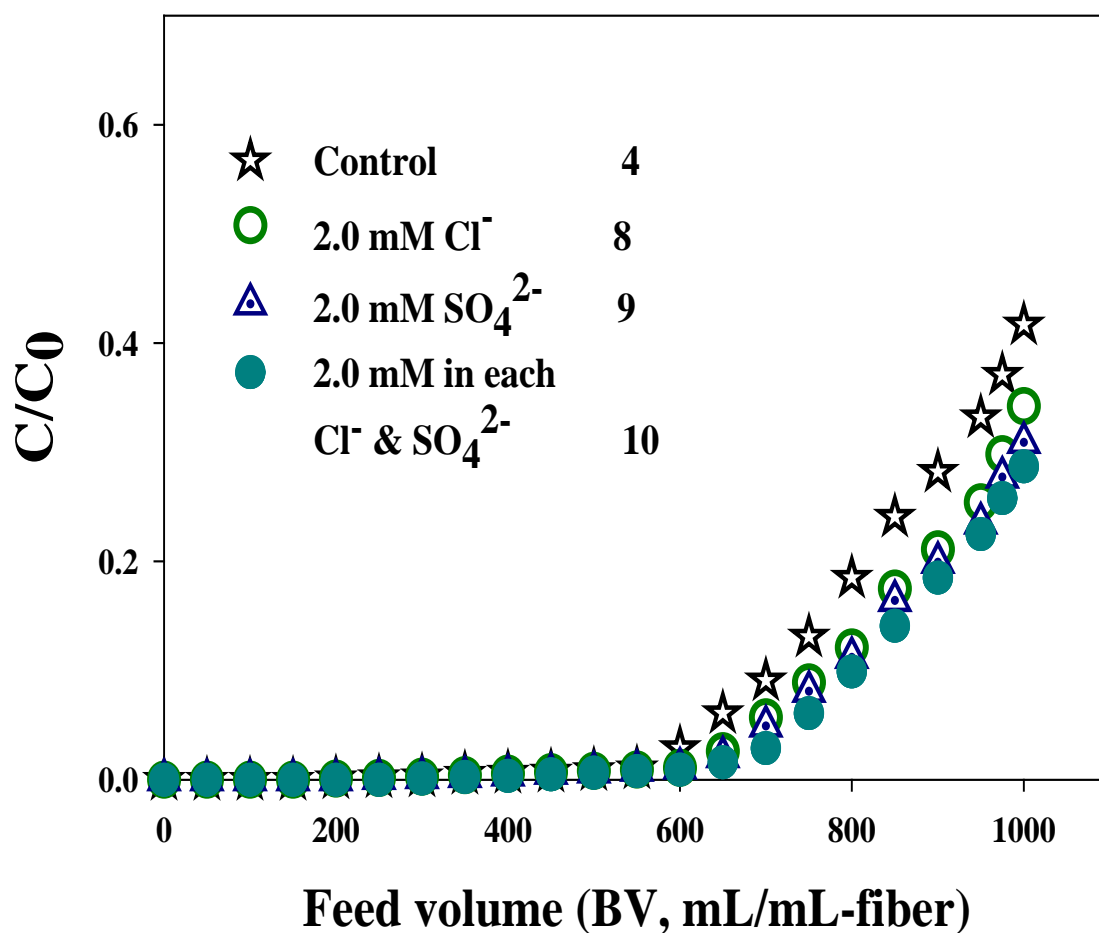


Fig. 3. Breakthrough profiles of phosphate adsorption by Zr-FCPS ligand exchange adsorbent in the presence of high concentration common anions. Figure for each symbol in the inset corresponds to entry nos. 4 and 8–10 in Table 2. For detailed conditions and numerical results refer to entry nos. 4 and 8–10 in Table 2.

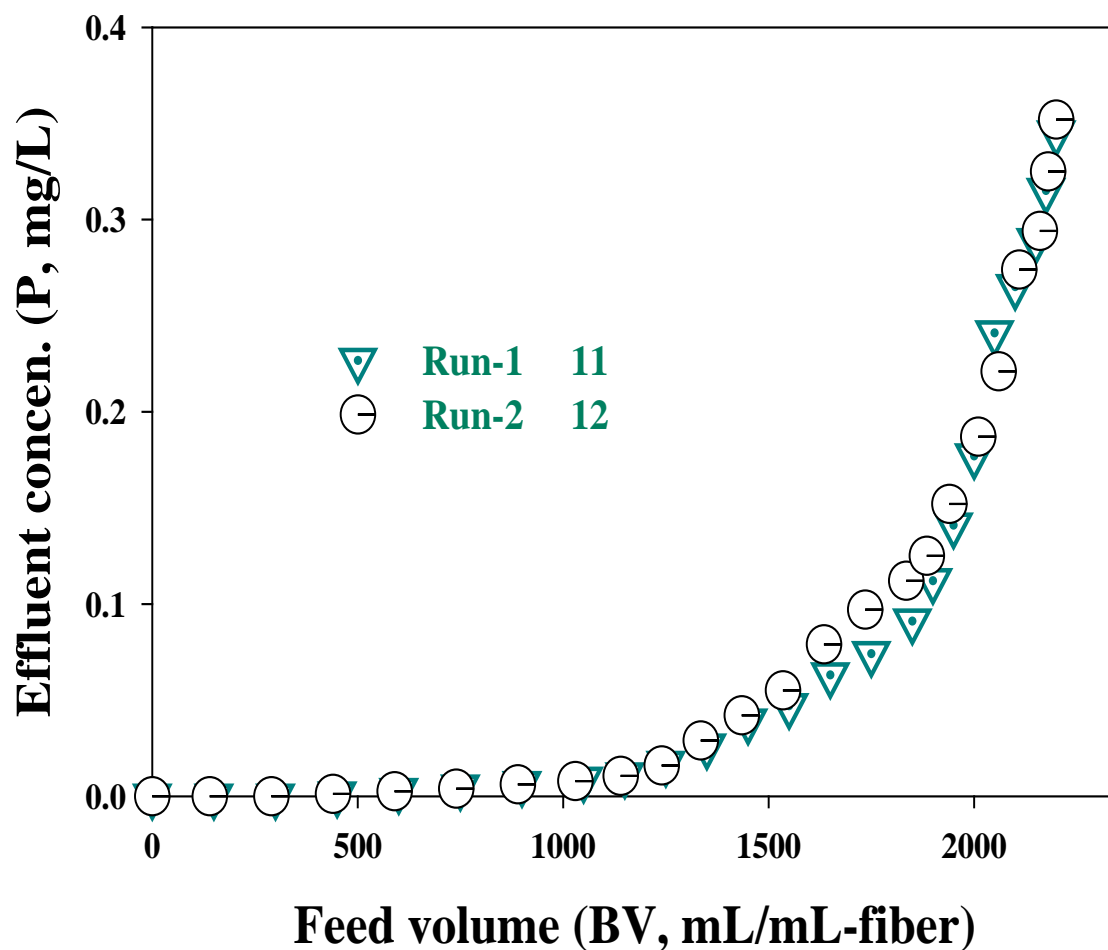


Fig. 4. Breakthrough profiles of phosphate adsorption at high feed flow rate of 850 h^{-1} . Feed solution concentration: phosphate was 0.014 mM and Cl^- and SO_4^{2-} was 2.0 mM in each. For detail conditions and numerical results refer to entry nos. 11 and 12 in Table 2.

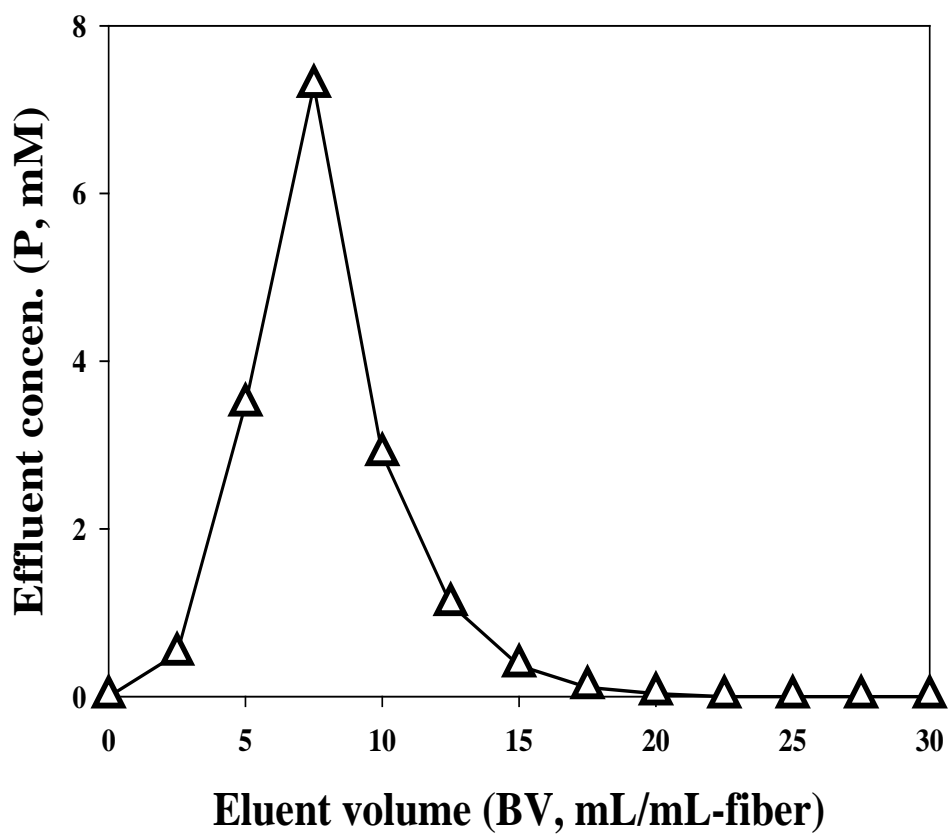


Fig. 5. Elution of adsorbed phosphate on Zr-FCPS column with 0.2 M NaOH at flow rate of 5 h^{-1} . For detailed conditions and numerical data of adsorption operation refer to entry no. 6 in Table 1.

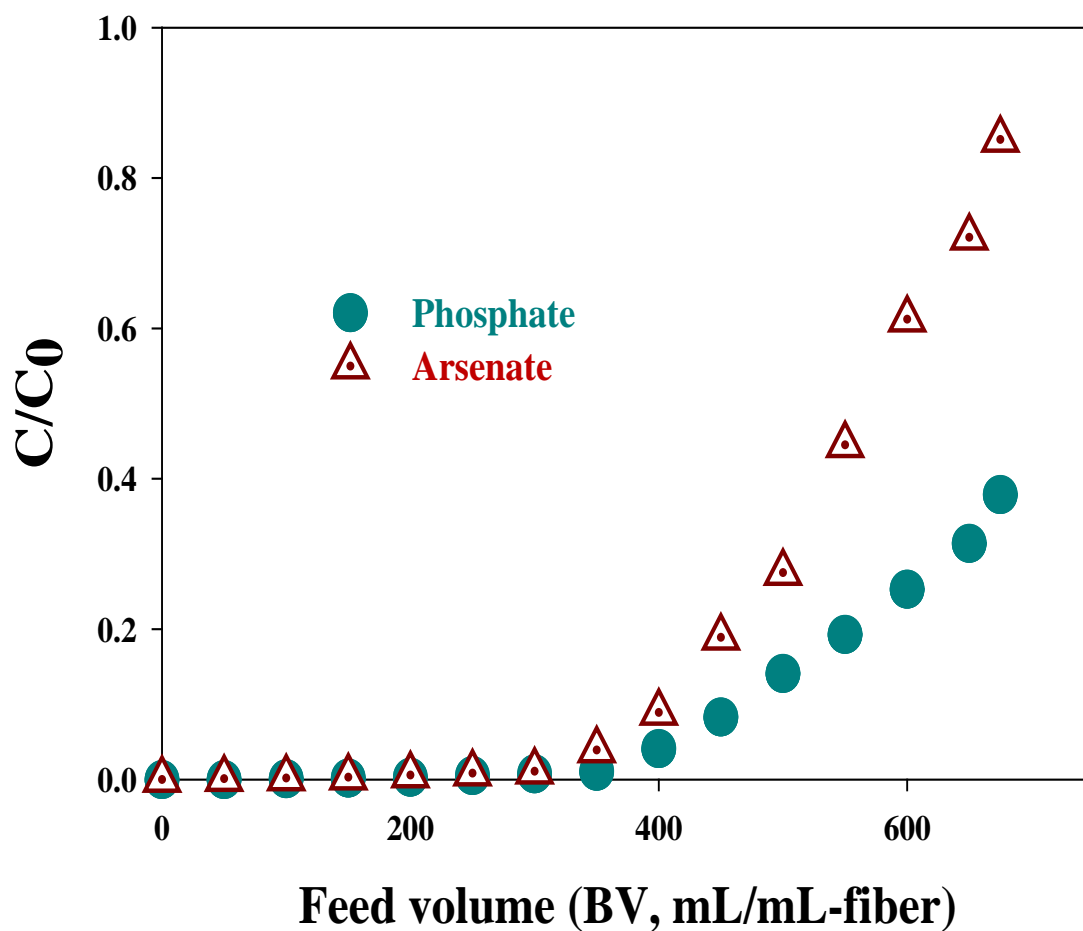
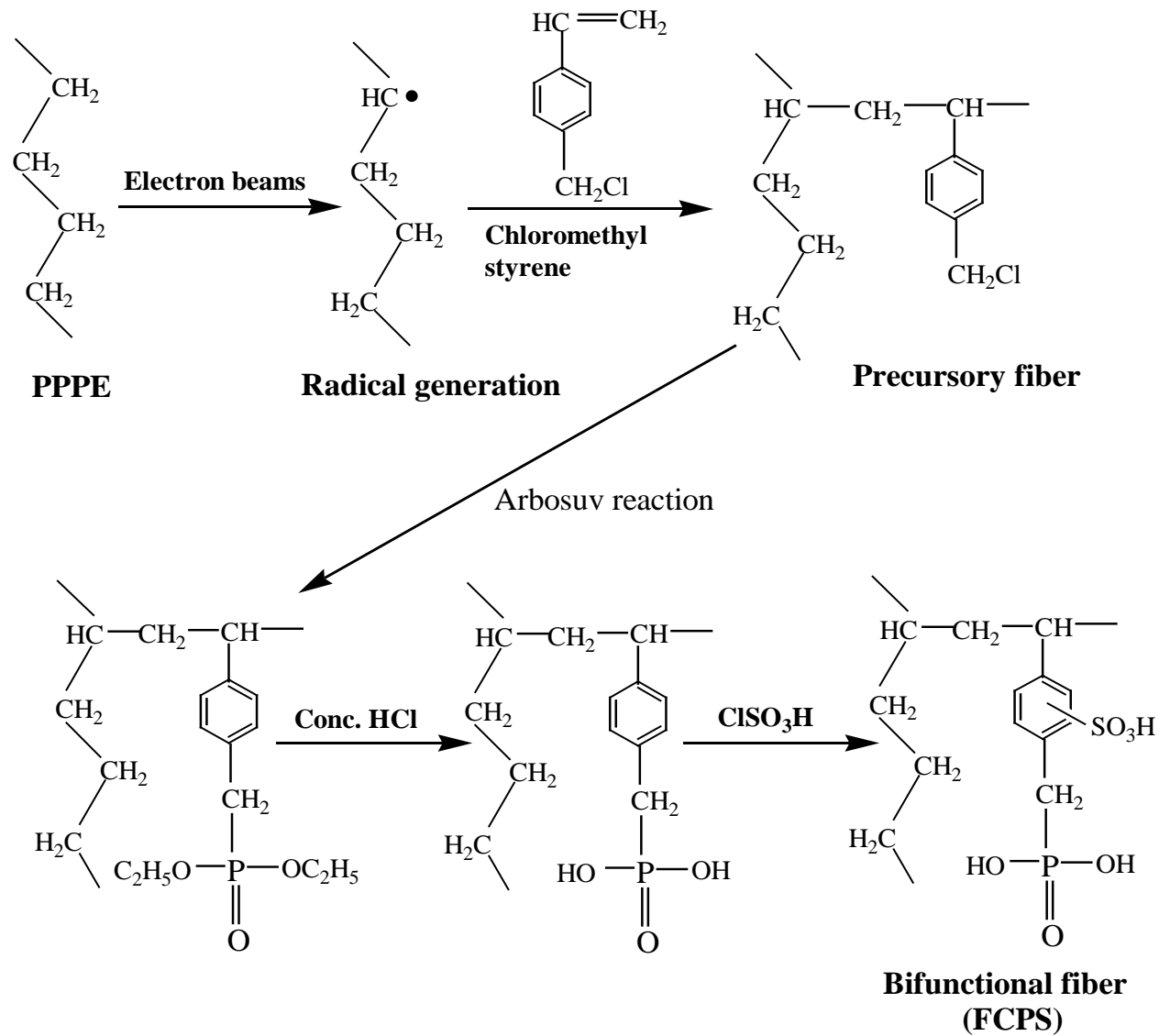
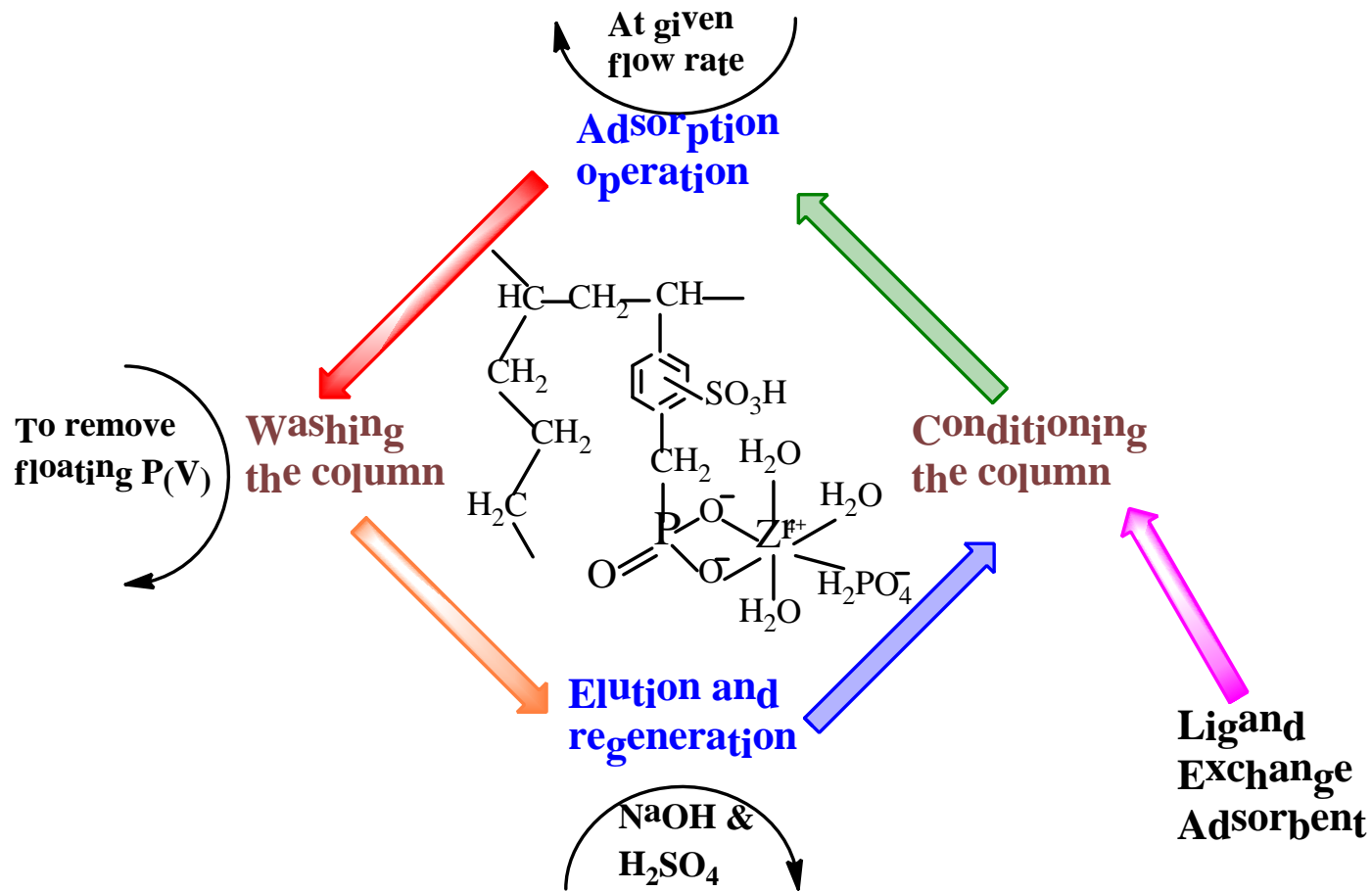


Fig. 6. Competitive adsorption of phosphate and arsenate by Zr-FCPS adsorbent. Feed solution containing both arsenate and phosphate was 0.0435 mM in each at pH 7.01 and flow rate 100 h⁻¹. For detailed conditions and numerical results refer to Table 3.



Scheme 1. Synthesis of bifunctional fiber containing both phosphonate and sulfonate groups (FCPS).

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31 **Scheme 2.** Possible bonding mechanism between Zr(IV) and FCPS (inside) and schematic illustration of reusability of ligand exchange
32 adsorbent for phosphate sorption, elution and regeneration process.