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Development of Arsenate and Phosphate Selective Adsorbents Having High Kinetic Performances

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September 2008
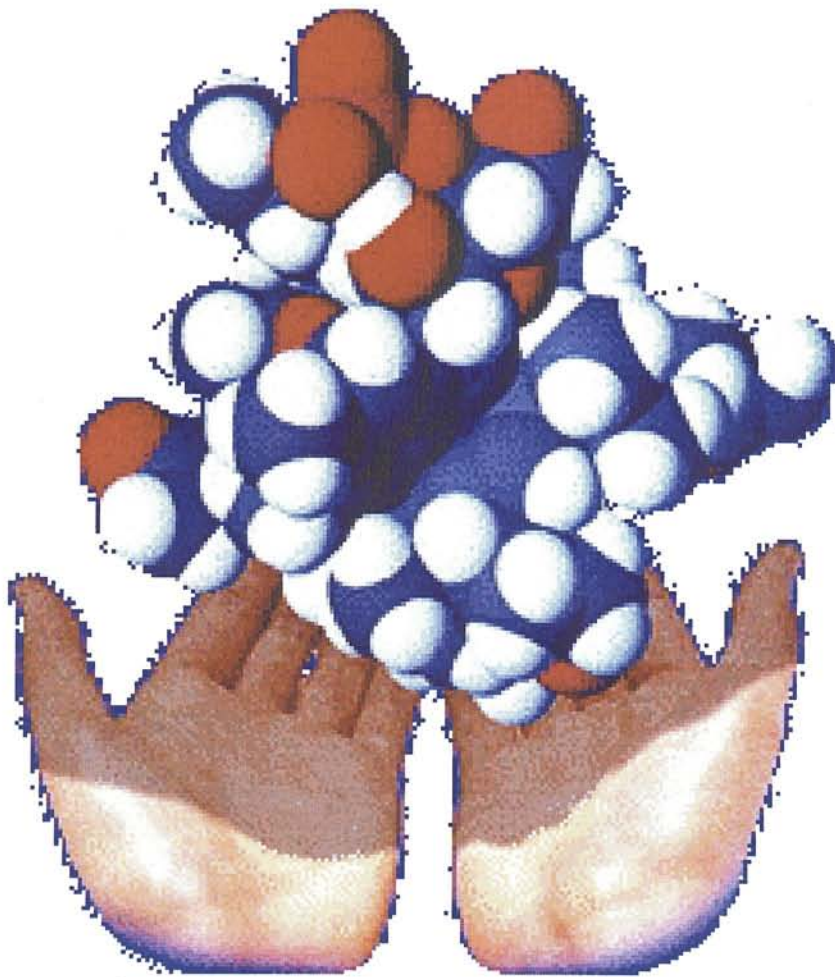
This dissertation was prepared in the Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, JAPAN under the supervision of **Professor Dr. Akinori JYO**.

To
My Little Son Rehan
And
Beloved Parents

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Chapter-1

1. Introduction

1.1. Arsenic and phosphate contamination in water and their toxicity

Man cannot live without pure drinking and safe water. In this case, when the water supply contains unsafe levels, the alternative step is to find out a safe source of drinking and cooking water. So, two options should be followed: removing contaminants from water and finding a new source of pure water. Therefore, drinking water must be in the standard levels, free from toxic elements, harmful bacteriological contamination and other chemical contaminants. This thesis will present the detailed investigation of arsenic and phosphate removal technologies, arsenate and phosphate removal from water by weak-base anion exchange fibers and resins containing primary amino group and highly selective Zr(IV) loaded adsorbents.

Arsenic contamination of groundwater has been called the largest 20th - 21st century mass poisoning calamity in human history (Chowdhury et al., 1999; Nordstrom D. K., 2002; Smedley and Kinniburgh, 2002; Brown and Ross, 2002; Chowdhury et al., 2000). Arsenic (As) ubiquitously presents in the environment in both organic and inorganic forms throughout the earth's crust and is usually found as compounds combined with some elements such as oxygen in the environment. However, arsenic combined with carbon and hydrogen is referred to as organic arsenic. Organic arsenic is less (about one tenth) toxic than inorganic arsenic. Inorganic arsenic-species in groundwater are usually in the form of arsenate (As(V)) and arsenite (As(III)). Arsenite is more toxic (40-60 times) for living organisms (Mudgal, 2005; Le, 2002).

On the other hand, huge volume of wastewater production is a great problem to natural environment and adversely affected to human beings, plants, and animals (Shin et al., 2004; Morse et al. 1998). The wastewater contents several toxic pollutants such as high amount of phosphorus and nitrogen and these nutrients are responsible for eutrophication problem of rivers, lakes and inland seas (Gachter and Imboden, 1985; Zhao and Sengupta, 1998). In addition, low concentration of phosphate caused the unexpected growth of algae in rivers, lakes and coastal bays. Before discharging high nutrient content wastewater into

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water bodies, removal of phosphate is important to conserve the natural aquatic environment. However, it is not completely practiced and causes problems globally.

Arsenic contamination in groundwater has been observed from many regions of the world such as Australia, New Zealand, Chile, Taiwan, Mexico, Mongolia, India, China, Vietnam, Thailand, USA, UK as well as Bangladesh as shown in **Figure 1-1** (Smedley and Kinniburgh, 2002). These occurrences are naturals and mining related. The World Health Organization has described arsenic in Bangladesh's wells as the largest poisoned calamity of human. According to recent statistics, it has been stated that fifty nine out of sixty four districts (85% of the total area) in Bangladesh and its 80 million people are at risk from arsenic poisoning (Karim, 2000). It is also estimated that about 30 million people are exposed to arsenic in water exceed 0.05 mg/L. Smedley and Kinniburgh (2002) reported that the arsenic problems of alluvial and deltaic aquifers of Bangladesh and West Bengal (India) in groundwater represent the most serious and the concentrations of arsenic in affected areas have a high amount range from 0.05 to 3.2 ppm as shown in **Figure 1-2**. However, Bangladesh has vast amounts of naturally occurring arsenic in its groundwater supply. The source of arsenic in Bangladesh is naturally occurring geological deposits. Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides, oxides, arsenites and arsenates, rock-forming minerals including sediments and soils (Smedley and Kinniburgh, 2002). The water is supply in rural area of Bangladesh by shallow and hand tube wells which are contained high concentration of arsenic. Depths of shallow and tube wells are usually 40-150 feet (Rashid and Mridha, 1998). On the contrary, surface water and groundwater from deeper aquifer is arsenic free and water supply in urban areas is usually from deep aquifers in Bangladesh and West Bengal. The rural people drink hand tube well water from shallow aquifers. Therefore, the rural people are more affected by arsenic contamination than urban people. In addition, arsenic contamination in developed countries comes from industrial discharges of impurities.

Figure 1-1- Distribution of documented world problems with arsenic in groundwater in major aquifers as well as water and environmenta problems related to mining and geothermal sources. Areas in blue are lakes.

Smedley P. L., Kinniburgh, D. G., 2002. Appl. Geochem. 17(5), 517–568.

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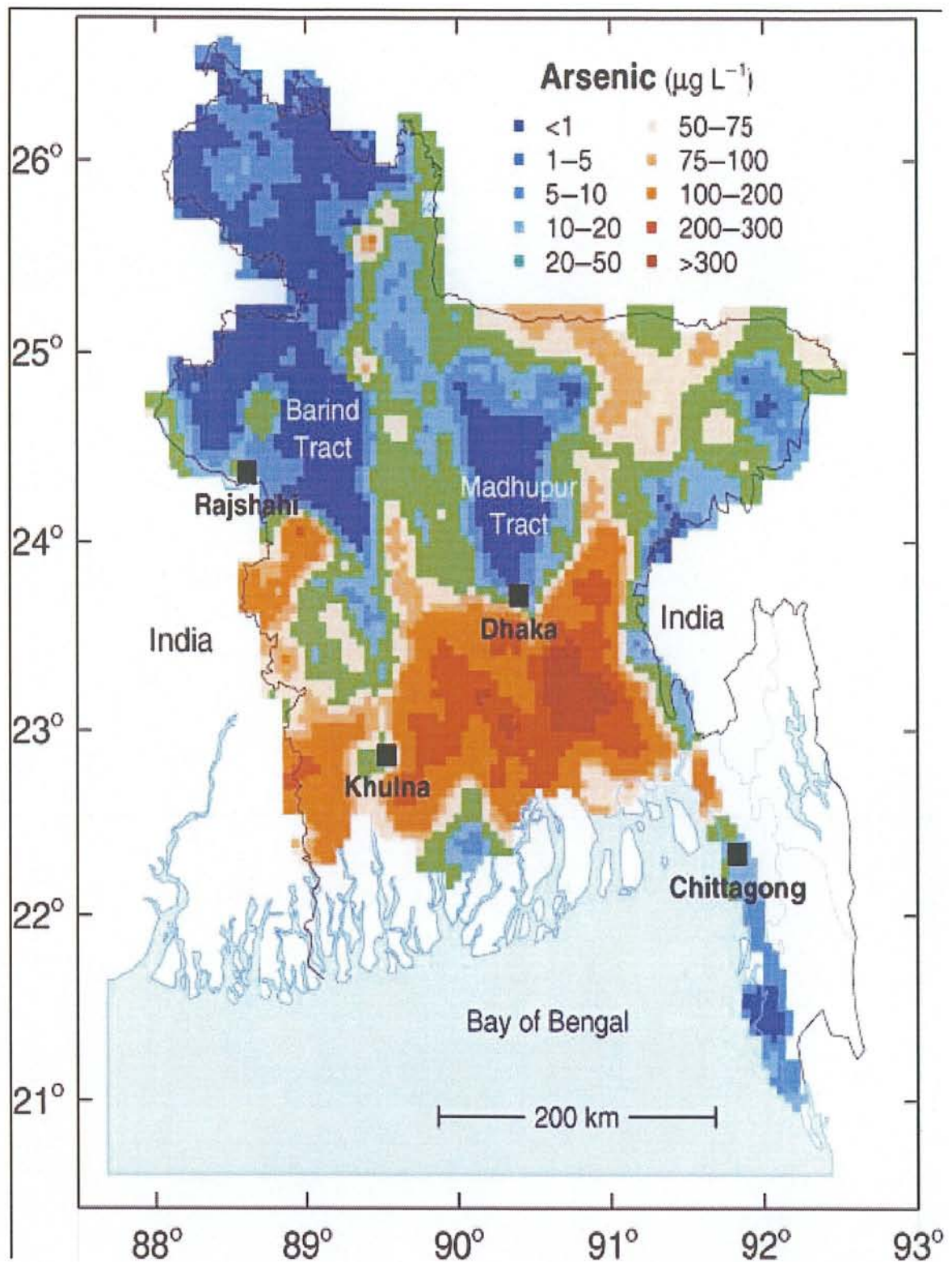
Figure 1-2- Smoothed map showing the distribution of arsenic in groundwater from shallow (<150 m) tube wells in Bangladesh.

Smedley P. L., Kinniburgh, D. G., 2002. Appl. Geochem. 17(5), 517–568.

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Arsenic toxicity is one of the most crucial global health problems affecting more than millions of people all over the world. Contamination is caused by arsenic from natural geological sources leaching into aquifers, contaminating drinking water and may also occur from mining and other industrial processes (Smedley and Kinniburgh, 2002). Any form of arsenic is toxic to human. Its toxicity is more than four times higher than that of the toxic trace element mercury (Rashid and Mridha, 1998). So the toxic effect of arsenic species depends on their chemical form, route of entry, age, sex, doses and duration of exposure and it is reported that arsenic toxicity occurs through contaminated food or drinking water or from accidental ingestion of insecticides (Chakraborti et al., 2003).

Arsenic occurs in two oxidation states: trivalent form of arsenite (As_2O_3; As(III)) and pentavalent form arsenate (As_2O_5; As(V)), and As(III) is sixty times more toxic than As(V) (Le, 2002). Arsenic is well documented human carcinogen affecting numerous organs. In vitro studies have indicated that arsenic can interfere with DNA replication, DNA repair and cell division. It has shown that arsenic can inhibit ligation of DNA strand breaks and if present during DNA synthesis, it can induce chromosomal aberrations, sister chromatid exchangers and malsegragation of chromosomes (Ratnaike, 2003). Arsenic toxicity is determined based on the ingestion of arsenic compounds and their excretion from the body and it is expected that 40-60% of arsenic is retained by human body and that is why the more arsenic containing water is summed up to the greater level of hazards (Karim, 2000).

Many countries have drinking water containing arsenic at more than World Health Organization (WHO) standard level. The two serious affected areas in the world are Bangladesh and West Bengal, India. In 59 districts in Bangladesh and in nine adjacent districts in West Bengal, 80 million and 42 million people respectively are exposed to groundwater arsenic concentrations that are above the WHO maximum permissible limit (Ratnaike, 2003; Karim, 2000). Bangladesh is one of the tropical countries and its water consumption is normally very high. Most of the affected regions are villages where people are involved in manual work in the crop production (Karim, 2000). The normal consumption of water for an adult in the village is estimated 5-6 liters per day. Villagers consume a lot of rice water in the morning and all the food is prepared using the arsenic contaminated water. So, villagers are ingesting more arsenic than anticipated.

Arsenic toxicity accounted in two ways of Acute and Chronic. Acute arsenic poisoning is associated initially with nausea, vomiting, abdominal pain, and severe

diarrhea. Moreover, encephalopathy and peripheral neuropathy also investigated. Chronic arsenic toxicity through drinking water results in multisystem human diseases (ATSDR, 2000). The clinical manifestation of chronic arsenicosis in human's effects of hyper- and hypo- pigmentation, keratosis, hypertension, cardiovascular diseases and diabetes and others are skin, lung and bladder cancers as shown some examples in **Figure 1-3** (Morales et al., 2000; Smith et al., 2000; Chakraborti et al., 2003). Cancers involving other organs have also been implicated.

Now it is important to remove arsenic from water to avoid the adverse health effects of human beings by giving arsenic free safe drinking water, because no effective medicine has been discovered to against arsenic toxicity. In this connection, the World Health Organization (WHO) established an international maximum contaminant level for arsenic in drinking water of 0.01 mg/L (IPCS (WHO), 1993; WHO, 2001). The United States Environmental Protection Agency (USEPA) and the European Union also set their maximum contaminant levels to 0.01 mg/L (USEPA, 2001). However, many countries are maintaining the standard level of arsenic is 0.05 mg/L, because of sufficient testing facilities and high cost of treatment.

The arsenic removal from water has drawn the kind attention of scientists and growing high interest because of negative health impacts to human beings as already discussed so far. Therefore, many researchers have been carried out their extensive research works to develop arsenic removal techniques based on cost effective, repeated use for long time and environmental friendly approaches. Many removal techniques have been proposed and adsorption by selective adsorbent is one of the most promising techniques because the adsorbents can use in simple technological method, rapid adsorption rate and repeatedly use without deterioration. Therefore, several methods will be discussed and make notes of advantages and disadvantages for the sake of comparison of removal methods. However, it will describe after a brief discussion of arsenic and phosphorus chemistry.

Figure 1-3- Patients exposed to arsenic contaminated water and diseases are (a) hyperkeratosis (b) arsenic lesions on hand (skin cancers) (c) suspected Bowen's disease, and nonhealing ulcers (suspected cancer) (d) arsenic lesions on feet (skin cancers)

1.2. Chemistry of arsenate and phosphate

Arsenic chemistry is complicated because it can exist in several forms in the environment and it toxicity depends on the arsenic species for existing. Arsenic exists in water primarily as oxyacids of arsenate (As(V)), arsenite (As(III)), and dominant organic forms are monomethylarsenate MMA, and dimethylarsenate DMA, (Smedley and Kinniburgh, 2002). However, arsenic was found in water mainly as trivalent (arsenite or As(III)) and pentavalent (arsenate or As(V)) forms. Arsenious acid is dissociated as follows (Ringbom, 1963):

$$H_3AsO_3 \rightleftharpoons H^+ + H_2AsO_3^- \qquad pKa_1 = 9.22$$
$$H_2AsO_3^- \rightleftharpoons H^+ + HAsO_3^{2-} \qquad pKa_2 = 12.1$$
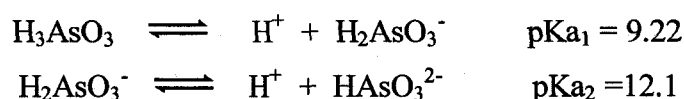
The trivalent arsenic is difficult to remove from water by using normally available separation process. Trivalent form change into pentavalent form by adding an oxidant such as chlorine and then removal process of arsenic was easy from water. Pentavalent form of arsenic acid is dissociated as follows (Ringbom, 1963):

$$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^- \qquad pKa_1 = 2.19$$
$$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-} \qquad pKa_2 = 6.94$$
$$HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-} \qquad pKa_3 = 11.50$$
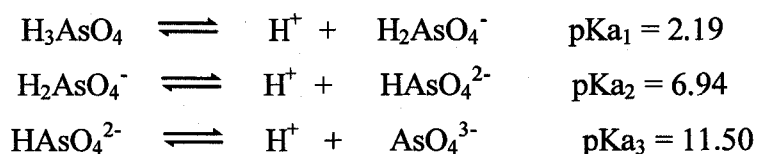
Because the pH range of municipal water supplies and ground water is from pH 6 to 9 and trivalent arsenic is found primarily as H_3AsO_3, which is not ionized. In the same pH range, on the other hand, pentavalent arsenic is found primarily as monovalent ($H_2AsO_4^-$) and divalent ($HAsO_4^{2-}$) forms. These forms of arsenic are more easily removed from water than trivalent arsenic. In the case of phosphoric acid, the dissociation constants as pKa are as follows (Ringbom, 1963):
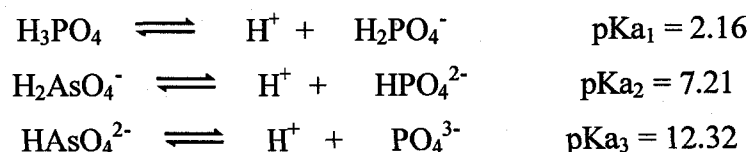
$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad pKa_1 = 2.16$$
$$H_2AsO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad pKa_2 = 7.21$$
$$HAsO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad pKa_3 = 12.32$$

Both parent acids, phosphoric and arsenic acids have very close values of pKa_1, pKa_2, and pKa_3. In addition, removal methods of phosphate are almost the same as arsenate. Therefore, arsenate removal is mainly described here.

1.3. Arsenic removal technologies

When an area's supplied water is completely affected by arsenic contamination, the safe water sources scare. It is essential to remove arsenic from the contaminated water within a short time. But it is difficult to remove arsenic in simple way if the concentrations more than 0.2 to 3.2 mg/L. Many technologies have been developed to remove arsenic from groundwater. Most of them are applied for small scale like households levels. It is reported that removal technologies have also removed the other undesirable compounds along with arsenic such as heavy metals, bacteria, turbidity, color, odor, hardness, nitrate, fluoride, silicate, ferrous and others metals depending on technology (Johnston and Heijnen, 2001). Coagulation and biological methods are used but they cannot remove arsenic completely near to zero or less than 0.01 mg/L level. Co-precipitation and filtration are the common methods for arsenic removal. But these are unable to remove arsenic efficiently. So other advanced treatments are ion exchange and adsorption by selective adsorbent or adsorption by granular metal oxides, activated alumina and membrane methods like reverse osmosis and nanofiltration. The major removal technologies are presented below:

1.3.1. Oxidation

Arsenite (As(III)) in surface water is not so high but in significant concentration level; the main species in surface water is arsenate (As(V)). On the other hand, both arsenate and arsenite in groundwater are high concentrations level. However, both groundwaters and surface waters in Bangladesh and West Bengal (India), arsenate and arsenite are large (Smedley and Kinniburgh, 2002). Oxidation alone is not able to remove arsenic from water and it will be cooperated with other processes, such as coagulation, filtration, and ion exchange. In this process, the chemicals oxidize or reduce to alter their

oxidation states. The trivalent form of arsenic (As(III)) is oxidized to pentavalent form of arsenic (As(V)). Arsenite is readily oxidized to arsenate by dissolved oxygen but the oxidation rate of dissolved arsenite by oxygen is extremely slow (Driehaus et al., 1995). Oxidants, such as chlorine, hypochlorite, ozone, potassium permanganate, manganese oxides, hydrogen peroxide, and Fenton's reagent were used to promote the oxidation rate (Kartinen and Martin, 1995; Driehaus et al., 1995; Walling, 1975). All oxidants have advantages and disadvantages and it should be account for choosing one of them to be used in this process. Chlorine, which has traditionally been used, is the rapid and effective oxidant of choice, but there are growing concerns for the generation of organochloride byproducts from the naturally occurring organic matters (Zaw and Emett, 2002). Potassium permanganate ($KMnO_4$) is available in developing countries where it was used as a topical antibiotic for minor cuts and it was stable with a long shelf life (Johnston and Heijnen, 2001). However, potassium permanganate has not produced any harmful by-products but may produce color in the water and cause filtration problems (Borho and Wilderer, 1996).

It has discovered that, in the presence of near-UV light and dissolved iron compounds; the oxidation rate of dissolved As(III) by air can be increased more than four orders of magnitude without using chemical oxidants; the oxidized arsenic can then be removed by an iron co-precipitation. A new advanced oxidation process developed which has more effective at neutral or alkaline pH states. Dissolved sulphur(IV) was used as a photo-absorber in an UV assisted sulfite oxygen process (Zaw and Emett, 2002; Clifford et al., 1986) for all techniques of As(V) removal. They investigated that iron-based photo-oxidation process had successfully used to oxidize and to remove arsenic from mine water. So the added iron acts as an oxidants as well as a coagulant. The oxidation of As(III) to As(V) provides an additional benefit by producing more stable solids for safe disposal.

Other chemicals have high possibilities for oxidation of As(III) include ferric chloride, hydrogen peroxide/Fe^{2+} (Fenton's reagent), and ferrate(VI) (Sharma et al., 1997; Sylvester et al., 2001). Both in developed and developing countries, Fenton's reagent (H_2O_2 in the presence of Fe^{2+} catalyst) is used as oxidant. It is known to be a powerful oxidizing agent because of the generation of OH radical (Walling, 1975).

$$Fe^{2+} + H_2O_2 \rightleftharpoons Fe^{3+} + HO^- + OH^\bullet$$

$$OH^\bullet + Fe^{2+} \rightleftharpoons Fe^{3+} + HO^-$$
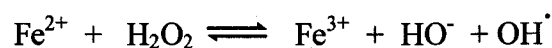
The hydroxyl radical is one of the most reactive chemical species. Fenton's reagent is used to treat a variety of industrial wastes containing toxic organic compounds, for organic pollutant destruction, toxicity reduction, and biodegradability, improvement of odor and color removal (Walling, 1975). Hydrogen peroxide may be an effective oxidant if the water contains high levels of dissolved iron which occurs in conjunction with arsenic contamination.

1.3.2. Co-precipitation and filtration

Co-precipitation and filtration include the alum coagulation, iron coagulation and lime softening. These methods are used to remove non-sedimentable colloidal solids and slow-settling suspended solids. However, colloidal particles are stable and not settled in reasonable time. Dissolved arsenic to form a low-solubility solid mineral such as metal arsenate and this solid is possible to remove by sedimentation and filtration. After adding coagulants, dissolved compounds such as arsenic can become insoluble and form solids. This process is known as co-precipitation. Co-precipitation and filtration are effective treatment processes for removal of arsenic according to laboratory and pilot-plant tests. This treatment can effectively remove many suspended particles besides arsenic, such as turbidity, iron, manganese and silicate (Johnston and Heijnen, 2001). Arsenic removal with these processes has been shown from a long time ago. The most commonly used salts are sodium hypochlorite, aluminum and ferric salts, such as alum and ferric chloride (Johnston and Heijnen, 2001; Meng et al., 2002).

Co-precipitation occurs when an inorganic contaminant like arsenic forms an insoluble complex such as metal hydroxide flocs with the coagulant. This process will transform soluble arsenic into insoluble reaction products (Gregor, 2001). For instance, arsenic containing water mixed with coagulants such as ferric or aluminum salts (chloride or sulfate), the reaction products as precipitated will be relevant ferric or aluminum hydroxide (Edwards, 1994; Hering et al., 1997). After addition of aluminum or ferric coagulants, soluble inorganic arsenic species converted into insoluble products by precipitation, co-precipitation or adsorption onto hydroxide phase or solid oxyhydroxide surface (Sancha, 2000; Legault et al., 1993). Therefore, insoluble products along with arsenic will be removed by sedimentation and filtration or gravity settling processes. The

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household co-precipitation and filtration method was proved reliable and easy to use.

These mechanisms can independently contribute towards contaminants removal. Precipitation has not been shown an important role for arsenic removal. So, both co-precipitation and adsorption are active arsenic removal mechanisms (Johnston and Heijnen, 2001). Many researchers have shown the importance of filtration to remove efficiently arsenic from water. Several researchers investigated that the co-precipitation and sedimentation achieved arsenate removal is 30% without filtration (Meng et al., 2001; Hering et al., 1997) and after filtration, the efficiency was improved to over 97%. It is also reported that household filtration process could effectively remove arsenic from Bangladesh well water, and estimated chemical costs are less than US$4 annually for family if daily consumption of 50 L of filtered water (Meng et al., 2001).

Co-precipitation or coagulation has some limitations. Mainly, it discharged huge amount of toxic sludge which can be difficult to manage and causes secondary environmental problem (Xu et al., 1998) and in addition, the process has no continuous flow system to remove arsenic from water (Kartinen and Martin, 1995). Moreover, chloride, sulfate, nitrate, silicate, fluoride and bicarbonate in arsenic containing water were dramatically decreased adsorption of arsenic. In particular, silica decreases the removal efficiency of As(V) with increasing aqueous silica concentrations and pH (Johnston and Heijnen, 2001; Meng et al., 2001; Davis et al., 2001).

1.3.3. Activated alumina

Activated alumina (AA) is a granulated form of porous aluminum oxide (Al_2O_3) and is thermal hydration of aluminum hydroxides ($Al(OH)_3$). AA has a tremendous specific surface area (200-300 m^2/g) for the removal of contaminants (Mugdal, 2005; Johnston and Heijnen, 2001). This has been used to remove cations and anions such as arsenic, fluoride, chromium, zinc, iron, phosphate and organic materials from contaminated water (Mugdal, 2005). In addition, AA is a common and commercial adsorbent material for water treatment and especially for the use of arsenic removal from water than other adsorbents. Its maximum adsorption capacity is 5 to 24 (mg As adsorbed/g media) (Ghosh and Yuan, 1987; Wasay et al., 1996a). In this treatment

process, the water containing arsenic passes through a cartridge of AA. The alumina adsorbs the arsenic and treated water is passed to the faucet. An AA cartridge combined with an activated carbon filter produces a good and broad-range water treatment plant.

Clifford (1999) reported that the mechanisms of arsenic removal are similar to those of a weak-base ion exchange resin, and are often collectively referred to as adsorption; through ligand exchange and chemisorptions are technically more appropriate. The kinetics of arsenic removal onto the alumina surface is slower than those of ion exchange resins, and some arsenic leakage is often noted in AA system. Adsorption sites on the AA are also attractive to a number of anions other than arsenate. Clifford (1999) also reported the selectivity sequence to anions of AA in the pH range of 5.5 to 8.5 as

$$OH^- > H_2AsO_4^- > Si(OH)_3O^- > HSeO_3^- > F^- > SO_4^{2-} >$$
$$CrO_4^- \gg HCO_3^- > Cl^- > NO_3^- > Br^- > I^-$$
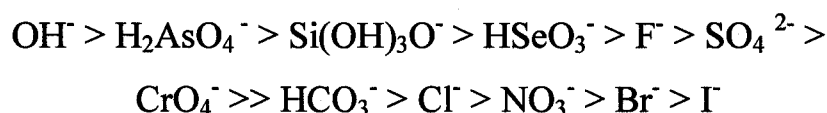
Some researchers included phosphate as the second most preferred anion, but AA exhibits the high selectivity for arsenate; competing anions pose fewer problems than with ion exchange resins (Trussell et al., 1980). Phosphate and fluoride are also adsorbed onto AA, producing improvements in drinking water quality, but at the same time reducing arsenic removal potential. In Bangladesh and West Bengal (India), the groundwater contains both As(III) and As(V) and therefore it is necessary to adopt a treatment process that removes both of the species of arsenic. Arsenic(V) will be predominant in aerobic surface water, whereas As(III) will be predominant in anaerobic groundwater. Mudgal (2005) indicated that As(III) can be removed effectively by AA bed without oxidizing it into As(V). The main disadvantage of AA is that it cannot regenerate completely after adsorption operation and alumina loses about 30-40% of its capacity with each regeneration operation. In addition, AA needs to be replaced after three or four regenerations (Kartinen and Martin, 1995) and it required backwashing before use to load in a reactor (Ghosh and Yuan, 1987).

1.3.4. Membrane processes

The membrane processes include coagulation/microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED). In these processes, dissolved molecules pass through or retain or excluded depend upon pore size, shapes and charges of compounds (Taylor and Wiesner, 1999). Membrane filtration has the advantage for removing many contaminants from water, including bacteria, salts and various heavy metals (Johnston and Heijnen, 2001). To use the membrane for arsenic removal, water must be free from suspended materials. The membrane processes could be effective to remove arsenic from water (Sato et al., 2002; Vrijenhoek and Waypa, 2000). MF and UF processes excluded water from particles greater than 0.1 μm. Membranes for use under low pressure have larger pore sizes and those for use under high pressure are smaller pores (Han et al., 2002). Separation of smaller ionic species by NF and RO membranes are dependent on the membrane properties, such as membrane charges and radii of pores. Membranes with smaller pores are able to retain ionic species and highly charged membranes exclude co-ions. Developments in membrane technology led to RO and NF membranes with high selectivity and large water flux under lower operating pressures. Arsenate is usually present in natural water as $HAsO_4^{2-}$, and is removed by NF and RO membranes (Vrijenhoek and Waypa, 2000). Arsenate removal of 97 % was achieved using thin-film composite *FilmTec* NF-70 membrane and 90 % removal of both As(V) and As(III) (90 %) was achieved by thin-film composite *FilmTec* NF-90 membrane (Sato et al., 2002). RO membrane process was also used in arsenic removal. For instance, removal efficiency for As(V) is more than 95% or greater for As(V) compared to ED (Huxstep and Sorg, 1988). RO membrane process was effective for a shorter life time for removal of As(III) than processes based on activated alumina and ion exchange (Clifford and Lin, 1991).

1.3.5. Ion exchange resins and related adsorbents

Adsorption by selective adsorbent, in particular, ion exchange process is more widely used than others because the process is simple. Then, this is usable for small household scales as well as large industrial ones. Ion exchangers are able to regenerate after adsorption and elution operations for repeated use. At the present, many synthetic ion

exchange and chelating resins can be commercially available. Most of these resins are based on polystyrene crosslinked with divinylbenzene. Recently, fibrous adsorbents having excellent kinetic performances have been reported, and some of them are now commercially available.

Commercially available anion exchange resins based on crosslinked polystyrene matrices do not exhibit high selectivity to dihydrogen arsenate or dihydrogen phosphate because of high hydrophobic nature of their polymer matrices. Therefore, these resins prefer less hydrated anions to highly hydrated counterions so long as counterions have the same charge number. For instance, selectivity sequence of strongly basic anion exchange resin for univalent inorganic anions is as follows (Wheaton and Bauman, 1951):

For Dowex-1 (I type anion exchange resin)

$$F^- < OH^- < H_2PO_4^- < HCO_3^- < Cl^- < NO_2^- < Br^- < NO^{3-} < HSO_4^- < I^-$$
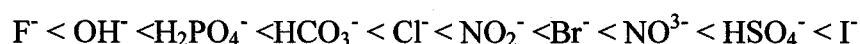
For Dowex-2 (II type anion exchange resin)

$$F^- < H_2PO_4^- < HCO_3^- < OH^- < Cl^- < NO_2^- < Br^- < NO_3^- < HSO_4^- < I^-$$
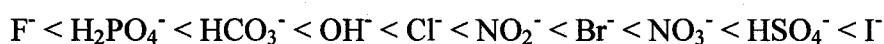
This sequence is nearly coincides with that of liquid anion exchanger (Shean and Sollner, 1972) and is called Hofmeister series. These studies suggest that development of anion exchange resins selective to both phosphate and arsenate are very difficult to achieve so long as copolymer matrices are hydrophobic (polystyrene crosslinked with divinylbenzene). Since no anion exchange resin having aliphatic crosslinked polymer matrices without any aromatic moieties has been commercialized yet, the selective removal of both arsenate and phosphate by commercialized resins is difficult to conduct.

Therefore, arsenate and phosphate selective adsorbents have been proposed by many researchers. Copper(II)-doped materials have a high affinity for arsenate (Ramana and Sengupta, 1992). Several researchers also developed Zr(IV) loaded phosphoric acid adsorbent to remove As(V) and As(III) (Zhu and Jyo, 2001a; Seko et al., 2004; Suzuki et al., 2000a). Suzuki et al. (2000b) studied the behaviors of porous resin loaded with crystalline zirconium oxide in the adsorption of As(V) and As(III). The maximum capacity was found 1.5 and 1.2 mmol/g for As(V) and As(III), respectively. A novel phosphoric

acid resin hiving high acid capacity and phosphorus content has been developed (Jyo et al., 1997). The chemical structure of phosphoric acid resin is shown in **Scheme 1-1**.
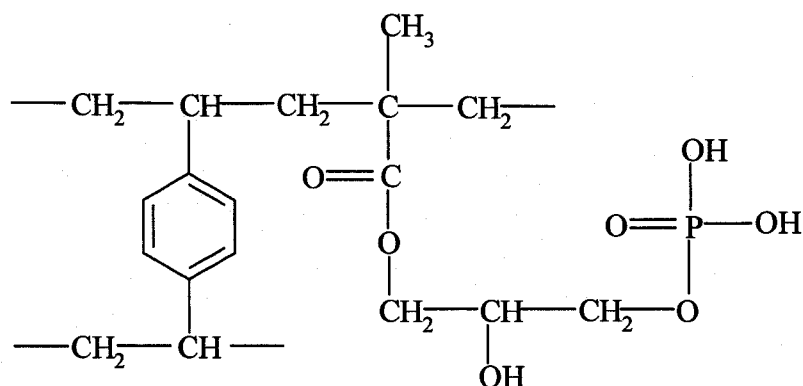
Scheme 1-1- Phosphoric acid resin

Zhu and Jyo (2001a) studied the removal of As(V) by Zr(IV) loaded phosphoric acid chelating resin by columnar mode and the maximum capacity for As(V) was 0.67 mmol/g of dry resin. They reported that this was one of most promising adsorbents for simultaneously removal of both As(III) and As(V) based on Zr(IV) loaded phosphoric acid resin. However, these ligand exchangers do not have kinetically excellent performances. Then, it is necessary to improve kinetic performances of ligand exchange adsorbent.

1.3.6. Alternative methods

Last several years, many researchers have been developed technologies for removing arsenic based on low-cost simple technique. These can be applied to small scale household equipments for removal of arsenate in rural areas. A few alternative methods have been investigated for arsenic removal. Many researchers reported about metallic iron adsorbent which is a unique adsorbent because of its high reactivity in water via spontaneous corrosion (Lackovic et al., 1998). However, Fe(0) is cheaply available and non-toxic but the corrosion rate control may be difficult in large scale application. Arsenic

adsorption by metallic iron adsorbent was interfered with phosphate, silicate, carbonate, nitrate, chromate, and molybdate and low interference for As(III) removal caused by borate or sulfate (Su and Puls, 2001). The groundwater in Bangladesh and India contains excess iron along with arsenic and this situation may be taken account to remove arsenic. The iron is present in the groundwater as ferrous iron and under appropriate redox and pH conditions, ferrous iron is readily oxidized to ferric state resulting in ferric hydroxide precipitate, which will remove arsenic by adsorption. High arsenic removal capacities were observed when iron concentrations are high in water (Mamtaz and Bache, 2001). Therefore, this method may be useful but there is no details information about correlation between arsenic and iron concentrations in groundwater.

Biological methods are useful to remove arsenic from water. Arsenic was removed from surface waters by phytoplankton. Phytoplankton both removes arsenic by biological uptake and the organisms or phytoplankton can act simply as particulate organic matter which adsorbs arsenic and settles organisms (Faye and Diamond, 1996). However, the arsenic removal from water by biological treatment has yet to be demonstrated. Instead of central water treatment, many scientists focused on small scale in home treatment in developing countries due to the view point of cost using available local materials and simple operation method. Some of adsorbents were developed for this purpose, including rice husk, coal, and coconut shell and few field results of household devices have shown to be promising results. A simple three-pitcher (locally known as "3-Kalshi" filter) filtration method is made by local materials. This method was tested for removing arsenic from groundwater in Bangladesh. In 3-kalshi assembly. The first has iron chips and coarse sand, and the second kalshi has wood charcoal and fine sand. The third is the collector of filtered water. By this process, arsenic was removed by ca. 95 % from raw water and this system is promising for use in rural areas because of the low cost of materials and simple operation technique (Khan et al., 2000). Meng et al. (2001) reported the removal of arsenic from well water based on the principles of co-precipitation and filtration. For convenient application of the chemicals, approximately 2 g of combined ferric chloride and sodium hypochlorite salts were sealed in small plastic packets. Each packet of chemicals could treat 20 L of well water with arsenic concentration of 0.05 mg/L or less and arsenic remaining in filtered water ranged from 1.9 to 21.8 µg/L, which is lower than standard levels of many developing countries. However, these processes caused another environment problem after dumping used materials.

1.4. Objectives of the present research

The main objectives of this study are to develop promising adsorbents and to evaluate performances of developed novel adsorbents for arsenate and phosphate removal from water. Therefore, aims of this study are as follows:

1. Development of both fibrous and resinous adsorbents and evaluation of their possibility for removal of arsenate and phosphate from water.

2. Evaluation of breakthrough capacities for uptake of arsenate and/or phosphate under various conditions (flow rates of feeds, compositions of feeds and so on)

3. Evaluation of the reusability of the adsorbents from the view point of long term use.

4. Investigation of behavior of adsorbents in removal of arsenate and phosphate from their trace concentration levels at high feed flow rates.

5. Comparison of kinetic performances of the developed adsorbents with those of related adsorbents.

1.5. Importance of the present research

The arsenic poisoning is one of the worst episodes in the world. Undoubtedly, arsenic and phosphate may aggravate human health and/or environment if appropriate measures are not taken to stop its spread. About the arsenic problem, Bangladesh is strongly facing difficulties with arsenic contaminated water with 59 districts out of 64 districts but their effective purification processes did not completely established due to the inefficiency of the separation methods and the lack of research in this arena. Although many technologies have been proposed to treat water containing arsenic but their adsorption rates are not high enough at high feed flow rates. Therefore, arsenic adsorbents having much higher adsorption rate must be developed to purify huge volumes of arsenic contaminated underground water within reasonable time. Recently, we have reported some promising fibrous adsorbents for simultaneous removal of both arsenate and phosphate at an extremely high feed flow rate such as weak-base anion exchange fibrous adsorbents and zirconium(IV) loaded ligand exchange adsorbents with extremely rapid adsorption rates based on the electron beam irradiation induced graft polymerization techniques. These

fibrous adsorbents can be purified low concentration of huge volumes of arsenate contaminated groundwater as well as phosphate within a reasonable short time.

1.6. Delimitation

This thesis is to elucidate the synthesis of weak-base anion exchange fiber and Zr(IV) loaded bifunctional fibers containing both phosphate and sulfonate by electron irradiation methods, and their application to remove arsenate and phosphate from water. In addition, poly(allylamine) resin in hydrochloride form and Zr(IV) loaded monophosphonic acid resin were also investigated to remove arsenate and phosphate from water. This work concisely clarifies the current removal techniques and compared the developed adsorbents with others adsorbent according to the scientific and practical viewpoints. The developed adsorbents are promising and usable for long time. Therefore, cost will be not a serious barrier to use these kinds of adsorbents in practical cases.

Chapter-2

Arsenate and phosphate removal from water by a weak-base anion exchange fibrous adsorbent

2.1. Arsenate removal

2.1.1. Introduction

Arsenic (As) contamination of groundwater occurs in many regions, and that in Ganges delta areas is most serious (Chakraborti et al., 2003; Smedley and Kinniburgh, 2002; Ratnaike R. N., 2003; Karim M. M., 2000). USEPA finalized that the maximum As contamination in drinking water is 10 µg/L (USEPA, 2001). Several technologies were proposed to the purification of drinking water (groundwater) contaminated with As. Among them, ion exchange processes are attractive for arsenic removal because repeated use of ion exchangers is possible (Kartinen and Martin, 1995). Highly arsenate selective adsorbents of ligand exchange type were reported; they were prepared by loading metal ions or metal oxides onto various ion exchangers (Chanda et al., 1988; Zhu and Jyo, 2001a; Suzuki et al., 2000a; An et al., 2005; Cumbal and SenGupta, 2005; Greenleaf et al., 2006; Vatutsina et al., 2007). However, their adsorption rates of arsenate are not always rapid and the rapid removal of arsenate from solutions as low as 1 mg of As/L level was not reported (Seko et al., 2004). Commercially available anion exchange resins, which are crosslinked polystyrene having chemically fixed quaternary ammonium groups or amino groups, do not have the high selectivity to arsenate species over chloride and sulfate. Crosslinked copolymer matrices of these resins are hydrophobic and they prefer lowly hydrated anions to highly hydrated ones so long as charge number of anions is equal. For instance, commercially available anion exchange resins exhibit the following selectivity sequence for monovalent anions: $OH^- \approx F^- < H_2PO_4^- < HCO_3^- < Cl^- < HSO_3^- < Br^- < NO_3^- < I^- < ClO_4^-$ (Aveston et al., 1958; Wheaton and Bauman, 1953). This order coincides with the decreasing order of free energy of hydration of anions (Leontidis, 2002) and also Hofmeister anion series (Shean and Sollner, 1972; Schulthess et al., 1985). In this connection, the anion coordination chemistry on complexation of cyclic polyammoniums

[–(CH$_2$-CH$_2$-NH$_2$$^+$)$_n$–] with multivalent anions clarified that these polyammonium ions bind strongly with multivalent anions, such as HPO$_4$$^{2-}$ and CO$_3$$^{2-}$ with high basicity but not strongly with monovalent anions, such as Cl$^-$ and NO$_3$$^-$ with low basicity (Dietrich et al, 1981; Kimura et al., 1982a; Hosseini and Lehn, 1982). This concept led us to development of an anion exchange fiber, in which hydrophilic polymer chains [-(CH$_2$-CH(NH$_2$))$_n$-] are grafted onto polyolefin fibers in order to obtain an anti-Hofmeister type anion exchanger.

In this work, therefore, we have prepared a novel fibrous anion exchanger of non-ligand exchange type for rapid and selective removal of arsenate from water based on electron irradiation induced graft polymerization technique (Lee et al., 1996; Saito et al., 1989) according to **Scheme 2-1**. This paper describes preparation of the weak-base anion exchange fiber FVA, its selectivity to arsenate species over chloride and sulfate evaluated by batchwise method, and its extremely rapid uptake of arsenate species in column-mode.

2.1.2. Experimental

2.1.2.1. Materials

As trunk fiber, two types of polyethylene coated polypropylene fibers (PPPE) were used. One was a filamentary fiber (named PPPE-f, diameter 12 μm, length 3.8 cm) and the other non-woven cloth of PPPE (named PPPE-c, diameter 15 μm). These fibers were provided by Kurashiki Textile Manufacturing Co., Osaka, Japan. N-Vinylformamide (98%) was obtained from Sigma-Aldrich Japan Co., Tokyo, Japan. Ultra-pure water prepared by a Milli-Q Academic-A10 (Nippon Millipore Co., Tokyo, Japan) was used throughout. Other chemicals were guaranteed grade unless otherwise specified.

2.1.2.2. Preparation of weak-base anion exchange fiber (FVA)

The fiber FVA was prepared according to reactions shown in **Scheme 2-1**. Each step will be mentioned below in detail.

2.1.2.2.1. Electron irradiation onto PPPE-c and PPPE-f

Fiber samples (PPPE-c or PPPE-f) were packed into polyethylene bags and the air in the bags was substituted with nitrogen. The fiber samples in the bags were exposed to
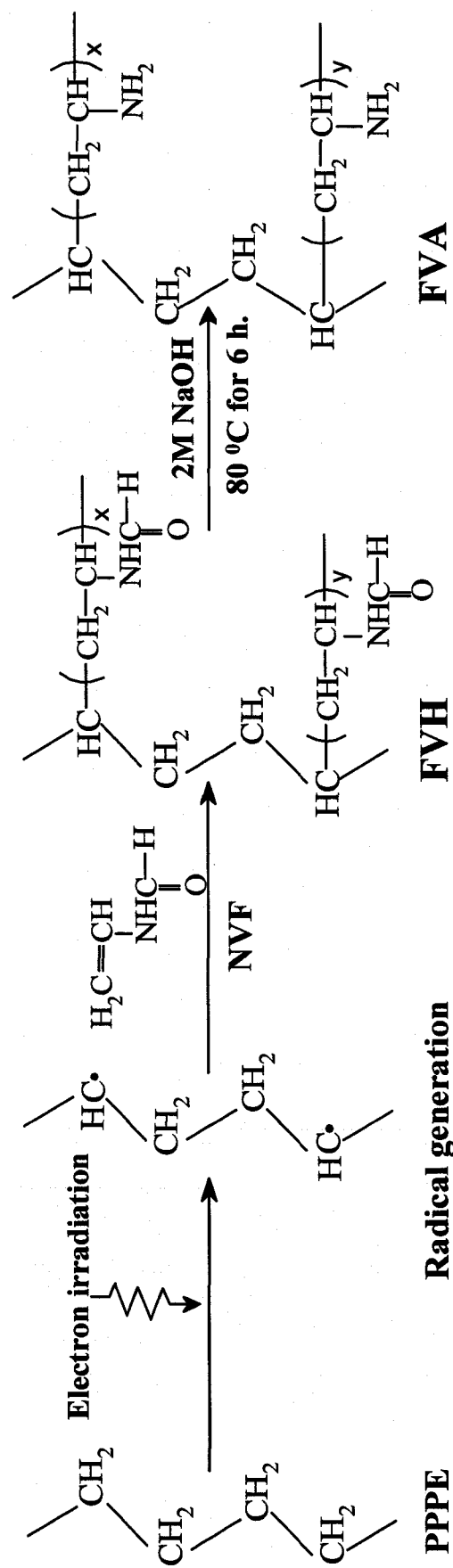
Scheme 2-1- Synthetic route of the anion exchange fiber with primary amino groups.

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electron beam (2 MeV) up to the total dose of 200 kGy. The electron irradiated fibers were stored in refrigerator at -80 °C under nitrogen atmosphere.

2.1.2.2.2. Graft polymerization of N-vinylformamide

After the inhibitor, o-phenylenediamine, in N-vinylformamide (NVF) was eliminated by distillation under reduced pressure, a methanol solution of NVF (30 wt%) was prepared. Then, nitrogen gas was bubbled into this monomer solution to expel dissolved oxygen for 20 min. Electron irradiated fibers were taken into a glass ampoule and the ampoule was fixed on a vacuum line. After the air in the ampoule was removed, the monomer solution was injected into the ampoule through vacuum line. Then, the ampoule was taken from the vacuum line and was stood in a water bath for a given time at 40 °C. After the graft polymerization reaction, NVF-grafted PPPE-c and PPPE-f were washed with water and dried in vacuum desiccators. The degree of grafting (Dg in %) was calculated from Eq. (1):

$$Dg = 10^2 (W_g - W_t)/W_t \qquad (1)$$

Here, W_t and W_g stand for weights of fibers before and after graft polymerization, respectively. The NVF-grafted PPPE-c and PPPE-f were named FVH-c and FVH-f, respectively.

2.1.2.2.3. Hydrolysis of formamide moieties in FVH-c and FVH-f

Both FVH-c and FVH-f were heated in 2 M sodium hydroxide solution at 80 °C for 6 h to change formamide moieties to primary amino ones. The resulting weak-base anion exchange fibers were washed with water and dried in vacuum after air-drying. The anion exchange fibers derived from FVH-c and FVH-f were named FVA-c and FVA-f, respectively.

2.1.2.3. Characterization of FVH and FVA

FVH and FVA were characterized by recording their IR spectra using a Spectrum One FT-IR spectrophotometer (PerkinElmer Instruments Ltd., Norwalk, CT, USA). CHN

analyses of FVH and FVA were conducted by Engineering Research Equipment Center, Kumamoto University.

2.1.2.4. Batchwise adsorption of arsenate

The weak-base anion exchange fiber of the non-woven cloth type (FVA-c) was treated with 1 M sodium hydroxide to convert to free amine form and washed with water until washing became alkali-free in column-mode. After air-drying, the fiber was dried in vacuum. Thus, FVA-c was used as in the free amine form. Diaion SA10A (strong-base anion exchange resin) was conditioned by a conventional method, and it was used as chloride form. A series of 0.010 M arsenate solutions of various pH values were prepared by mixing 0.010 M arsenic acid solution with 0.010 M disodium hydrogenarsenate solution at pertinent volume ratios. These test solutions (25 mL) were taken into a series of Erlenmeyer flasks (50 mL) and then FVA-c in the free amine form or Diaion SA10A in the chloride form (0.050 g of each) were added to the flasks. Thereafter, all flasks were shaken in a water bath with a mechanical shaker at 30 °C for 24 h. Then, concentrations of As in supernatants were determined by means of ICP-AES. Determination of As will be described in detail in a later section. Uptake of As in mmol/g-dry of adsorbent was calculated by the equation $(C_{initial} - C_{eq})(25/0.050)$. Here, $C_{initial}$ and C_{eq} stand for initial and equilibrium concentrations of As in supernatants, respectively. Values of equilibrium pH were also measured.

2.1.2.5. Column-mode adsorption and elution of arsenate

A sample of dried FVA-f (0.50 g) was packed into a polyethylene column (inner diameter 1.30 cm) and the fiber was swollen with water for 24 h. Then, the fiber bed was carefully pressed with a glass rod with flat end until the bed height became constant. The volume of the wet FVA-f bed in the column was 2.40 mL, which was used as reference volume in conversion of volume of feeds to bed volumes (BV) and also flow rates in mL/h to space velocity (SV). 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 a flow rate of a solution or water in mL/h and V_{bed} is the reference volume of the fiber bed in mL. Volumes of all solutions or water

supplied to the columns in adsorption-elution-regeneration operations were expressed by BV, which is designated by the ratio, $V_{supplied}/V_{bed}$; here $V_{supplied}$ is a volume of a feed supplied to the column in mL. Hydrochloric acid (1 M) was passed through the column at a flow rate of 20 h^{-1} in SV to convert the free amine form to the ammonium one. This made it possible to adsorb anionic species by FVA-f. Then, water (42 BV) was fed to the column at a flow rate of 20 h^{-1} in SV to eliminate free hydrochloric acid from the column.

Feeds containing arsenate were prepared by dissolving disodium hydrogenarsenate in water. In adsorption operation, flow rates of feeds were changed from 100 to 1050 h^{-1} in SV. After each adsorption operation, the column was washed with 42 BV of water and the adsorbed arsenate was eluted with 1 M hydrochloric acid at a flow rate of 20 h^{-1} in SV. After the elution of arsenate, the column was washed with 42 BV of water for the next run. The 1% breakthrough point was defined by the volume of a feed up to $C/C_o = 0.01$. Here, C and C_0 represent concentrations of As in column effluents and feeds, respectively.

2.1.2.6. Determination of arsenic by means of ICP-AES

The ICP-AES instrument and its attachment used were a CID Plasma Photoemission Spectrophotometer IRIS (Nippon Jarrell Ash Co., Kyoto, Japan) and Hydride Generator HYD-10 (Nippon Jarrell Ash Co., Kyoto, Japan), respectively. Analysis of As in all solutions was performed at a wavelength of 193.7 nm according to the calibration curve method. An As standard solution (1000 mg of As/L, As_2O_3 and NaOH in water and then pH 5 with HCl) for the instrument calibration was purchased from Wako Pure Chemical Industries Co., Osaka, Japan. This was diluted with water to be pertinent concentrations. When concentrations of As in test solutions were higher than 5 mg of As/L (batch-mode study and column-mode study for entry nos. 1 – 6 in **Table 2-2**), the calibration of the instrument was carried out by using three standard solutions containing 0, 8.00, and 16.0 mg of As/L. For instance, the linear least squares calibration curve obtained by using these standard solutions was linear with a correlation coefficient of higher than 0.9999. Linear least squares analysis of calibration data showed that the lower detection limit was less than 0.1 mg of As/L. When concentrations of As in solutions were beyond the calibration range, these solutions were exactly diluted with water down to the concentration of As to be less than 16.0 mg of As/L. When concentrations of As in

feeds used in the column-mode study were lower than 2 mg of As/L (entry nos. 7 - 10 in **Table 2-2**), arsine generation apparatus was attached to the ICP-AES instrument to enhance the sensitivity of As. Here, the calibration was conducted in the concentration range between 0 and 2.2 mg of As/L and/or between 0 and 1.2 mg of As/L. For instance, linear least squares analysis of calibration data showed that calibration curves obtained by using standard solutions of 0, 0.60, 1.20 mg of As/L were linear with correlation coefficients of higher than 0.9999 and the lower limit of the detection was less than 0.009 mg of As/L. In this work, sample solutions having complicated matrices were not used, and then no significant interference of matrices was observed.

2.1.3. Results and discussion

2.1.3.1. Characterization of FVA-c and FVA-f

Table 2-1 lists the nitrogen contents of NVF-grafted PPPEs (FVH-c and FVH-f) and the resulting weak-base anion exchange fibers FVA-c and FVA-f. The Dg value of FVH-c is slightly greater than that of FVH-f, although both FVH-c and FVH-f were prepared under almost the same grafting conditions. Main difference in properties between two trunk fibers PPPE-c and PPPE-f is in their diameters. Diameter of the former (15 μm) is slightly greater than that of the latter (12 μm). These results probably mean that the efficiency of radical generation on the fibers is affected by diameter of the fibers. However, the real cause for this difference in the Dg values is not clear at the present stage. In FT-IR spectra of both FVH-c and FVH-f, strong adsorption bands of amide carbonyl groups were observed around 1650 cm^{-1}. FVA-c and FVA-f, which were obtained by hydrolysis of FVH-c and FVH-f, respectively, did not exhibit the strong absorption bands of the amide carbonyl groups, whereas medium NH$_2$ deformation band was observed at ca. 1600 cm^{-1}. A nitrogen content of FVH-f was 4.6 mmol/g and that of FVA-f was 7.1 mmol/g. The nitrogen content of FVA-f increased as a result of hydrolysis reaction as expected. On the contrary, the nitrogen content of FVA-c decreased from that of FVH-c. This probably means that cleavage of some grafted chains from the trunk polymers occurred during hydrolysis of FVH-c because of its too high Dg value, which sometimes led to such unfavourable phenomena.

Table 2-1- Nitrogen contents of N-vinylformamide grafted fibers and the resulting anion exchange fibers having primary amino groups in the free amine form

Fiber	Symbol for fiber [a]	Nitrogen content (mmol/g)
N-Vinylformamide grafted fibers	FVH-c (145%)	7.3
	FVH-f (112%)	4.6
Anion exchange fibers having primary amino groups	FVA-c	6.4
	FVA-f	7.1
Strong-base resins	Diaion SA10A	3.6

[a] Suffixes –c and –f mean non-woven cloth and filament types, respectively. Figures in parentheses are degree of grafting (Dg). FVA-c and FVA-f in free amine form. Diaion SA10A in chloride form.

2.1.3.2. Batchwise study

2.1.3.2.1. Uptake of arsenate species from solutions containing arsenate species only

Arsenic acid is triprotic acid and dissociates as follows (Ringbom, 1963):

$$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^- \quad pKa_1 = 2.19$$
$$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-} \quad pKa_2 = 6.94$$
$$HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-} \quad pKa_3 = 11.50$$
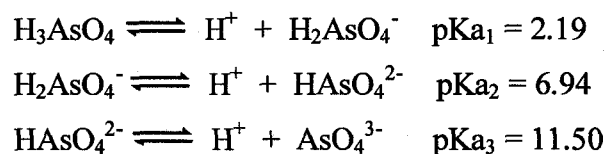
In the batchwise study, the free amine form of FVA-c was contacted with solutions of pH values from 2.31 to 6.90 prepared by mixing 0.010 M arsenic acid with 0.010 M disodium hydrogenarsenate. Then, uptake of arsenate species by FVA-c can be expressed as follows:

$$\overline{F-NH_2} + H_3AsO_4 \rightleftharpoons \overline{F-(NH_3)^+ \cdot H_2AsO_4^-} \quad (2)$$

$$\overline{2F-NH_2} + H_3AsO_4 \rightleftharpoons \overline{(F-(NH_3)^+)_2 \cdot HAsO_4^{2-}} \quad (3)$$

$$\overline{F-NH_2} + H_2AsO_4^- \rightleftharpoons \overline{F-(NH_3)^+ \cdot HAsO_4^{2-}} \quad (4)$$
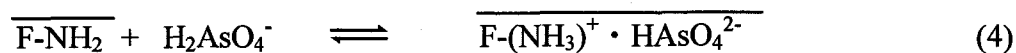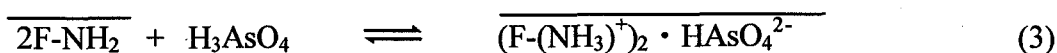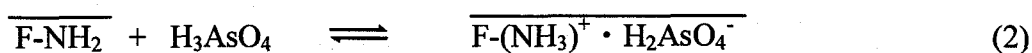
Thus, arsenate species are taken up as monovalent and divalent anions by protonated positive sites. **Figure 2-1(a)** shows uptake of arsenate species as a function of the equilibrium pH. With an increase in the equilibrium pH, uptake of arsenate species decreases. This indicates clearly that arsenate species is adsorbed in the form of monovalent anion below pH 4.6 (= (pKa_1 + pKa_2)/2). In the case of weak-base anion exchange resins, amounts of protonated sites gradually decrease with an increase in pH (Helfferich, 1962). In addition, divalent anionic species of arsenate increases with an increase in pH value above pH 4.6. Because of convolution of these two phenomena, uptake of arsenate gradually decreases with an increase in pH. **Figure 2-1(a)** also shows uptake of arsenate species by Diaion SA10A in the chloride form as a function of equilibrium pH of solutions. Strong-base anion exchange resins such as Amberlite IRA 900 and IRA 958 ($R-N^+(CH_3)_3$· Cl^-) do not have the high selectivity toward arsenate species (An et al., 2005); its uptake is not so high as that of FVA-c. In addition, uptake of arsenate species by Diaion SA10A was not markedly dependent on pH of solutions since anion exchange capacity of strong-base anion exchange resins is essentially independent of pH of solutions. In ligand exchange type adsorbents, uptake of arsenate also decreased with an increase in pH (Seko et al., 2004; Suzuki et al., 2000a; Vatutsina et al., 2007).

2.1.3.2.2. Effect of foreign anions on uptake of arsenate species

Common anions dissolved in freshwater and groundwaters are chloride and sulfate. The effect of these anions on uptake of arsenate was studied in the equilibrium pH range from 2.26 to 7.90. **Figure 2-1(b) and (c)** show effect of chloride and sulfate on uptake of arsenate, respectively. As judged from **Figure 2-1(b)**, equimolar chloride did not strongly interfere with uptake of arsenate species by FVA-c, which took up arsenate species by more than 0.97 mmol/g below pH 7.90. On the other hand, arsenate uptake by Diaion SA10A was markedly affected by chloride, in particular, in the acidic pH region below pH 3.25, where uptake of arsenate by Diaion SA10A was less than 0.61 mmol/g.

In uptake of arsenate species by FVA-c, sulfate strongly interfered with uptake of arsenate below pH 4. Between pH 2 and 4.6, a dominant species of arsenate is monovalent anion ($H_2AsO_4^-$). According to electroselectivity (Helfferich, 1962), divalent anions are adsorbed by anion exchangers in preference to monovalent anions. Then, sulfate ion

strongly interfered with uptake of arsenate species by both FVA-c and Diaion SA10A below pH 4. Above pH 4.6, divalent arsenate species increases with an increase in pH leading to reduction of the interfering effect of sulfate. In the case of FVA-c, its maximum uptake of arsenate of 1.4 mmol/g was observed at pH 6.77. On the contrary, the maximum uptake by Diaion SA10A was only 0.36 mmol/g. The anion selectivity of FVA-c was quite different from that of Diaion SA10A, which is one of most popular quaternary ammonium type anion exchange resins. Opposed to the case of Diaion SA10A, FVA-c clearly prefers divalent arsenate species to sulfate. Since the basicity of divalent arsenate anion is much higher than that of sulfate, divalent arsenate can be bound through hydrogen bonding with F-(NH$_3$)$^+$ groups in addition to conventional electrostatic uptake with the fixed positive sites as schematically shown in **Scheme 2-2**. In this connection, Kimura et al. (1982b) have reported that complexation of polyammonium with carbonate ion enhances an apparent dissociation constant of bicarbonate ion. Triprotonated cyclic polyamines [16]aneN$_5$ and [17]aneN$_5$ (denoted as LH$_3$$^{3+}$) form stable complexes with carbonate ion with stability constants (K$_{comp}$) of ca. 10^4 as follows:

$$LH_3^{3+} + CO_3^{2-} \rightleftharpoons [LH_3^{3+} \cdot CO_3^{2-}] \qquad : K_{comp} \qquad (5)$$

The dissociation of bicarbonate ion is written as:

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad : Ka_2 \qquad (6)$$

Addition of Eqs. (5) and (6) gives Eq. (7), which represents the apparent dissociation of

$$LH_3^{3+} + HCO_3^- \rightleftharpoons [LH_3^{3+} \cdot CO_3^{2-}] + H^+ \qquad : Ka_{(app)} \qquad (7)$$

bicarbonate ion in the presence of LH$_3$$^{3+}$. Ka$_{(app)}$ can be represented by Ka$_2$K$_{comp}$, which is equal to ca. 10^{-6}. Then, Ka$_{(app)}$ becomes to be 10^4 times larger than dissociation constant of bicarbonate itself, i.e., 10$^{-10.32}$. In adsorption of arsenate species by polyprotonated FVA, maximum uptake in the presence of equimolar sulfate was observed at pH 6.77 **(Figure 2-1(c))**. This pH value is much less than pH 9.2 (= (pKa$_2$ + pKa$_3$)/2), where the distribution of HAsO$_4$$^{2-}$ species becomes maximum (ca. 100%). This means that the following

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complexation reaction (8) similar to Eq. (7) occurs and apparent dissociation constant $Ka_{(app)}$ of dihydrogenarsenate ion is probably enhanced as mentioned above.

$$\overline{2F\text{-}(NH_3)^+} + H_2AsO_4^{2-} \rightleftharpoons \overline{[(F\text{-}(NH_3)^+)_2 \cdot (HAsO_4^{2-})]} + H^+ \tag{8}$$

Figure 2-1(c) also means that complexed $HAsO_4^{2-}$ can not be easily expelled by sulfate which can not form stable complex with polyprotonated sites because its basicity is lower than that of $HAsO_4^{2-}$ as schematically explained in **Scheme 2-2**. Thus, sulfate significantly interferes with uptake of monovalent $H_2AsO_4^-$ by FVA-c but hardly the uptake of $HAsO_4^{2-}$ by FVA-c.

2.1.3.3. Column-mode study

In column-mode study, FVA-f in polyammonium form was used in uptake of arsenate as described in the experimental section. The protonation of primary amino groups in the fiber with hydrochloric acid can be shown by Eq. (9).

$$\overline{F\text{-}NH_2} + H^+ + Cl^- \rightleftharpoons \overline{F\text{-}(NH_3)^+ \cdot Cl^-} \tag{9}$$

Since dominant species of arsenate in the neutral pH region are monovalent anion ($H_2AsO_4^-$) and divalent one ($HAsO_4^{2-}$), it is estimated that arsenate species will be taken up through the following anion exchange reactions:

$$\overline{F\text{-}(NH_3)^+ \cdot Cl^-} + H_2AsO_4^- \rightleftharpoons \overline{F\text{-}(NH_3)^+ \cdot H_2AsO_4^-} + Cl^- \tag{10}$$

$$\overline{2(F\text{-}(NH_3)^+ \cdot Cl^-)} + HAsO_4^{2-} \rightleftharpoons \overline{(F\text{-}(NH_3)^+)_2 \cdot HAsO_4^{2-}} + 2Cl^- \tag{11}$$

Here, we have tested uptake of arsenate by feeding test solutions of pH ca. 7, and the arsenate concentration was varied from 0.014 mM (1.0 mg of As/L) to 1.32 mM (98.9 mg of As/L). **Figure 2-2** shows breakthrough curves of arsenate under conditions where flow rates were changed from 100 to 425 h^{-1} in SV and concentrations of arsenate were ranged from 0.15 to 1.32 mM. **Figure 2-3** does ones from the flow rate range from 590 to 1050 h^{-1}

in SV and the concentration range of feeds from 0.014 to 0.080 mM. Detailed experimental conditions are summarized in **Table 2-2** with numerical results. In this work, the flow rate of the feed increased with a decrease in the feed concentration. With a decrease in the feed concentration, the breakthrough point of arsenate increases as shown in **Table 2-2**. However, the breakthrough capacity decreases with a decrease in the concentration of arsenate in feeds. This is mainly due to the concentration of arsenate C_b at the breakthrough point decreases with a decrease in C_0 because of the definition $C_b = 0.01C_0$. Then, the absolute concentration of arsenate at the breakthrough point gradually decreases with a decrease in C_0 leading to gradual decreases in the breakthrough capacity.

Although contamination of huge volume water with high concentration levels of arsenate hardly occurs, that with trace arsenate concentrations does frequently. To purify huge volume water contaminated with a trace arsenate, a kinetically excellent adsorbent is practically important. Then, in this work, the flow rate of feeds increased with a decrease in arsenate concentration in feeds as summarized in **Table 2-2**. In case of entry nos. 10 in **Table 2-2**, for instance, the flow rate of the feed containing 0.014 mM of arsenate (1.0 mg of As/L) was 1050 h^{-1} in SV, which is equal to feed flow rate of 2520 mL/h (= 1050 mL/mL- fiber bed x 2.40 mL-fiber bed). Under these conditions, the breakthrough point is 4670 BV (BV = mL/mL-fiber bed). This means that the presented column can purify ca. 11.2 L of water contaminated with 1 mg of As/L down to less than 0.010 mg of As/L (WHO drinking water standard) for 4.4 h.

Figure 2-1- Uptake of arsenate as a function of equilibrium pH in the absence and presence of foreign anions. Exchangers: ● FVA-c, ■ Diaion SA10A (50 mg of each in dry state); solutions: 10 mM arsenate solution of various pH (25 mL); Equilibration: 30 °C for 24 h. (a) in the absence of foreign anion; (b) in the presence of 10 mM sodium chloride; (c) in the presence of 10 mM sodium sulfate.

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Scheme 2-2- Schematic illustration for the high selectivity of protonated FVA to arsenate. Since basicity of hydrogenarsenate ($HAsO_4^{2-}$) is much higher than that of chloride and sulfate, hydrogen bond (dotted line) formation occurs between hydrogenarsenate ($HAsO_4^{2-}$) and polyammonium groups ($F(NH_3)^+$) but not in the case of Cl^- and SO_4^{2-}.

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Figure 2-2- Breakthrough curves of arsenate in column-mode uptake of arsenate by FVA-f under different flow rates of feeds containing arsenate at various concentrations. Figure on each curve corresponds to entry nos. in Table 2-2. For detailed experimental conditions, refer to entry nos. 1, 2, 3, and 4 in Table 2-2.

Figure 2-3- Breakthrough curves of arsenate in column-mode uptake of arsenate by FVA-f under different flow rates of feeds containing arsenate at various concentrations. Figure on each curve corresponds to entry nos. in Table 2-2. For detailed experimental conditions, refer to entry nos. 5, 6, 7, 8, 9, and 10 in Table 2-2.

Table 2-2- Column-mode adsorption of arsenate by FVA-f during the different flow rates and concentrations of feeds

Entry no.	Flow rate of feed (h^{-1} in SV)	C_0 of arsenate in feed (mM)	Volume of feed (BV)	1% Breakthrough point (BV)	1% Breakthrough capacity (mmol/g)	Total uptake of arsenate (mmol/g)	Amount of eluted arsenate (mmol/g)	Recovery (%)
1	100	1.32	117	93	0.591	0.707	0.784	110
2	210	0.66	413	187	0.589	1.16	1.14	98
3	350	0.33	829	361	0.567	0.941	0.976	103
4	425	0.15	1663	703	0.514	0.874	0.904	103
5	590	0.080	3325	1264	0.487	0.890	0.928	104
6	625	0.078	3325	1204	0.456	0.892	0.964	108
7	675	0.025	4992	3096	0.384	0.576	0.626	108
8	950	0.026	4992	3025	0.371	0.564	0.612	108
9	1000	0.015	7492	5077	0.351	0.498	0.508	102
10	1050	0.014	7492	4670	0.298	0.480	0.516	107

pH of feeds: ca. 7.0 and fibers bed volume: 2.4 mL.

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Figure 2-4- Elution of arsenate adsorbed on the FVA-f column with 1 M hydrochloric acid. For detailed conditions of adsorption operation, refer to entry no. 10 in Table 2-2. Flow rate of eluent: 20 h^{-1} in SV.

The adsorbed arsenate was able to be quantitatively eluted with 1 M hydrochloric acid as shown in **Figure 2-4** according to the following reactions:

$$\overline{F\text{-}(NH_3)^+ \cdot H_2AsO_4^-} + H^+ + Cl^- \rightleftharpoons \overline{F\text{-}(NH_3)^+ \cdot Cl^-} + H_3AsO_4 \qquad (12)$$

$$\overline{(F\text{-}(NH_3)^+)_2 \cdot HAsO_4^{2-}} + 2H^+ + 2Cl^- \rightleftharpoons \overline{2(F\text{-}(NH_3)^+ \cdot Cl^-)} + H_3AsO_4 \qquad (13)$$

During the elution procedure, FVA-f in the column is simultaneously regenerated into the initial polyammonium form. Then, the FVA-f packed column can be used in the next adsorption operation after washing the column with water. Indeed, all results shown in **Table 2-2** were obtained using the same column for four months without change of the packed FVA-f.

2.1.4. Conclusions

The fibrous adsorbent containing primary amino groups FVA was prepared by electron beam irradiation induced graft polymerization of NVF onto polyethylene coated polypropylene trunk fibers and the subsequent alkali hydrolysis of formamide moieties on the grafted chains. FVA became an anion exchanger when the primary amino groups were polyprotonated. Batchwise study clarified that the polyprotonated FVA prefers arsenate species to chloride and sulfate in neutral pH regions, different from a traditional strong-base anion exchange resin, such as Diaion SA10A, which prefers chloride and sulfate to arsenate. This specific anion selectivity of the polyprotonated FVA can be ascribed to (1) the high hydrophilicity of grafted chains and (2) hydrogen bonding of divalent arsenate anion with fixed ammonium in addition to conventional anion exchange mechanism. The column-mode study clarified that the polyprotonated FVA was able to take up arsenate very rapidly from the feed containing arsenate. For instance, the polyprotonated FVA was able to take up arsenate from a dilute solution of arsenate as low as 1.0 mg of As/L at the extremely high feed flow rate of 1050 h^{-1} in SV. Under these conditions the breakthrough capacity of polyprotonated FVA for arsenate was 0.298 mmol/g and this breakthrough capacity means that 1.0 mL of wet protonated FVA can purify 4.7 L of water contaminated with 0.014 mM arsenate (1.0 mg of As/L) for ca. 4.4 h.

2.2. Phosphate removal

2.2.1. Introduction

Discharge of phosphate into the water causes serious adverse effects to natural aquatic environments. The trace amount of phosphate in lakes, bays, coastal areas, and inland seas is also liable for eutrophication. The low concentration of phosphate less than 1.0 mg/L caused the unexpected growth of algae in lakes and coastal bays (Gachter and Imboden, 1985; Zhao and Sengupta, 1998). For this reason, new mandate has been established for phosphorus reduction in wastewater effluent at 10 µg/L (Florida Everglades Forever Act, 1994; Hansen, 2006). Many techniques have been proposed for phosphate removal such as iron coagulation (Suzuki et al., 2002; Morse et al., 1998; Bektas et al., 2004; Yang et al., 2006), biological removal (Stante et al., 1997; Randall et al., 1997; Strickland, 1998; Kuba et al., 1993) and adsorption by selective adsorbents (Anirudhan et al., 2006; Sorm et al., 1996; Ruixia et al., 2002; Urano and Tachikawa, 1991; Zhao et al., 2000; Navarro et al., 1999; Hamoudi et al., 2007; Namasivayam et al., 2005; Chen et al., 2002). 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 (Randall et al., 1997; Strickland, 1998). 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 (Zhu and Jyo, 2005; Blaney et al., 2007; Chimenos et al., 2003; Genz et al., 2004; Fytianos et al., 1998; Lee et al., 2003; Shin et al., 2004; Seida and Nakano, 2002 Zhao and Sengupta, 2000; Chitrakar et al., 2006; de-Bashan and Bashan, 2004). Granular adsorbents, however, cannot efficiently take up anions in column-mode at high feed flow rates more than 50 h^{-1}. Among these techniques, adsorption by selective adsorbents is more economical for long term uses (Morse et al., 1998; Anirudhan et al., 2006; Urano and Tachikawa, 1991; de-Bashan and Bashan, 2004). In this regard, we have reported the weak-base fibrous anion exchanger named FVA for selective and rapid removal of arsenate from aqueous solutions (Awual et al., 2008). The FVA packed column was able to take up arsenate from a dilute solution of arsenate as low as 0.014 mM (1.0 mg of As/L) even at a high feed flow rate of 1000 h^{-1} with high efficiency. Furthermore, FVA is a rare organic anion exchanger, which prefers

arsenate species to chloride and sulfate. Of interest is therefore the behavior of FVA in uptake of phosphate, since chemical properties of phosphate very resemble those of arsenate. In this work, we have studied equilibrium uptake of phosphate with FVA as a function of equilibrium pH in the absence and presence of chloride or sulfate by means of the batch-mode approach and also studied behavior of FVA in column-mode uptake of phosphate under various conditions, in particular high feed flow rates up to $2500\ h^{-1}$.

2.2.2. Experimental

2.2.2.1. Materials

Two types of FVA were used. One is non-woven cloth type named FVA-c and the other filamentary type named FVA-f. Preparation of both FVA-c and FVA-f were reported in detail in section 2.1.2.2. **Table 2-3** lists some important properties of FVA-c and FVA-f in free amine form. For comparison, a strong base anion exchange resin Diaion SA10A in chloride form was used and provided by Mitsubishi Chemical Co., Tokyo, Japan. Ultra-pure water prepared by a Milli-Q Academic-A10 (Nippon Millipore Co., Tokyo, Japan) was used throughout. Phosphoric acid (85 wt%), $NaH_2PO_4 \cdot 2H_2O$ and $Na_2H_2PO_4 \cdot 12H_2O$ were guaranteed grade and were obtained from Wako Pure Chemical Industries Ltd., Osaka, Japan. Other chemicals used were guaranteed grade unless otherwise specified.

Table 2-3- Properties of anion exchange fibers with primary amino groups FVA and strong-base anion exchange resin Diaion SA10A

Exchanger	Symbol for exchanger [a]	Nitrogen content (mmol/g)
anion exchange fiber	FVA-c	6.37
anion exchange fiber	FVA-f	7.29
strong-base resins	Diaion SA10A	3.65

[a] Suffixes –c and –f mean non-woven cloth and filament types, respectively. FVA-c and FVA-f in free amine form. Diaion SA10A in chloride form.

2.2.2.2. Batchwise study

FVA-c was used as free amine form. Diaion SA10A was conditioned as described (Helfferich, 1962) and was used as chloride form. A series of 0.010 M phosphate solutions of different pH values were prepared mixing 0.010 M H_3PO_4, 0.010 M NaH_2PO_4, and/or 0.010 M Na_2HPO_4. Test solutions (25 mL) were taken into a series of Erlenmeyer flasks (100 mL), and then FVA-c in free amine form or Diaion SA10A (0.050 g of each) in chloride form was added to the flasks. All flasks were shaken in a water bath with a mechanical shaker at 30 °C for 24 h. 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).

2.2.2.3. Column-mode study

First, FVA-f in free amine form (0.50 g in dry state) was placed in a polyethylene column (inner diameter 1.3 cm) and swollen for 24 h in water. Then, FVA-f in free amine form was converted into hydrochloride form ($F-NH_3^+Cl^-$) as follows; 1 M HCl (100 mL) was supplied to the column at flow rate of 10 h^{-1} and then the column was washed with water (100 mL) at flow rate of 20 h^{-1}. 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. Feeds for removal of phosphate were prepared by dissolving $NaH_2PO_4 \cdot 2H_2O$ into water and their final pH was adjusted with dilute HCl or NaOH, when needed. Feeds containing phosphate were supplied to the column at a given flow rate. Prior to the elution operation, the column was washed with water (100 mL) at flow rate of 20 h^{-1}, and phosphate adsorbed on the column was eluted with 1 M HCl (100 mL) at flow rate of 10 h^{-1}. During this elution operation, the column was simultaneously regenerated into hydrochloride form. Then, 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 stand for concentrations of phosphate in feeds and column effluents, respectively. The breakthrough capacity of FVA-f for phosphate was designated as uptake of phosphate in mmol/g fiber up to the breakthrough point. All column effluents including washings

were collected on a fraction collector and phosphorus (P) concentration in each fraction was determined by ICP-AES.

2.2.2.4. Determination of phosphorus by means of ICP-AES

The ICP-AES instrument used were a CID Plasma Photoemission Spectrophotometer IRIS (Nippon Jarrell Ash Co., Kyoto, Japan). The phosphorus and arsenic standard solutions for calibration were purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan. Phosphorus concentration was analyzed at a wavelength of 213.6 nm according to the calibration curve method. The detail arsenic determination method was described in section 2.1.2.6. The instrument was calibrated using three standard solutions containing 0, 6.00 and 12.0 mg of P/L (for batch-mode study, column-mode study of entry nos. 1 - 14 in **Table 2-4**, entry nos. 19 - 26 in **Table 2-5** and entry nos. 27-28 in **Table 2-6**) and the correlation coefficient of calibration curve was higher than 0.9999. For the determination of trace concentration of phosphorus below 1 mg of P/L (entry nos. 15 - 18 in **Table 2-4**), the instrument was calibrated using standard solutions of 0, 0.60 and 1.20 mg of P/L and the correlation coefficient of calibration curve was also higher than 0.9999.

2.2.3. Results and discussion

2.2.3.1. Batchwise study

First, we would like to mention that FVA-c in free amine form was used to evaluate uptake of phosphate in the absence of competing anions as described in this section. **Figure 2-5(a)** shows dependence of phosphate uptake by FVA-c on equilibrium pH in the absence of competing anion. Here, phosphate uptake by Diaion SA10A is also shown for comparison. Initial pH of test solutions was 2.25 through 6.90. Phosphate uptake by FVA-c markedly decreases with an increase in pH but not so in case of Diaion SA10A. Because proton donating species in test solutions are H_3PO_4 or $H_2PO_4^-$ and FVA-c is initially in the free amine form, equilibrium pH markedly increased from the initial pH as a result of phosphate uptake by FVA-c. For instance, when initial pH values were 2.25 and 6.90,

equilibrium pH values attained 2.60 and 7.96, respectively. Therefore, phosphate uptake by FVA-c in the free amine form can be expressed by the following equations (1), (2), and (3):

$$\overline{\text{F-NH}_2} + \text{H}_3\text{PO}_4 \rightleftharpoons \overline{\text{F-NH}_3^+ \cdot \text{H}_2\text{PO}_4^-} \tag{1}$$

$$\overline{\text{2F-NH}_2} + \text{H}_3\text{PO}_4 \rightleftharpoons \overline{(\text{F-NH}_3^+)_2 \cdot \text{HPO}_4^{2-}} \tag{2}$$

$$\overline{\text{F-NH}_2} + \text{Na}^+ + \text{H}_2\text{PO}_4^- \rightleftharpoons \overline{(\text{F-NH}_3^+) \cdot \text{HPO}_4^{2-} \cdot \text{Na}^+} \tag{3}$$

Because pKa_1, pKa_2 and pKa_3 of phosphoric acid are 2.16, 7.21, and 12.32, respectively (Ringbom, 1963), H_2PO_4^- and HPO_4^{2-} are taken up by protonated sites of FVA-c. In uptake of anions, FVA-c must be protonated by accepting proton from H_3PO_4 and H_2PO_4^- species because FVA-c was initially free amine form. Since dominant species is H_2PO_4^- in pH 4.6 through 7.2, sodium ion must be taken up into the bulk of the fiber phase as shown in the equation (3) above pH 4.6. Phosphate uptake by FVA-c decreased with an increase in pH; this can be ascribed to combined effect of a decrease in protonated sites and an increase in the fraction of HPO_4^{2-} species with an increase in pH. It is well known that fraction of protonated sites of weak-base resins decreases with an increase in pH (Helfferich, 1962). In case of Diaion SA10A, equilibrium pH did not so markedly differ from initial ones, since no acid-base reaction occurs in uptake of phosphate by the strong-base resin in chloride form. Below pH 4.6, however, anion exchange inactive species H_3PO_4 increases with a decrease in pH, and in particular, H_3PO_4 becomes a primary species below pH 2.16 (= pKa_1). Then, the decrease in phosphate uptake becomes rather marked around pH 2.16. In the neutral pH region around pH 7, dominant species are H_2PO_4^- and HPO_4^{2-} and more preferred divalent HPO_4^{2-} is taken up by expelling chloride in the resin phase. Then, uptake of phosphate by Diaion SA10A does not decrease different from the case of FVA-c even at nearly neutral pH of 6.6. However, uptake of phosphate by Diaion SA10A is less than that by FVA-c below pH 8.

Chloride and sulfate are main anionic species in rivers. Then, their effect on uptake of phosphate was examined. **Figures 2-5(b)** and **2-5(c)** show uptake of phosphate as a function of equilibrium pH in the presence of chloride and sulfate, respectively. The chloride little interferes with uptake of phosphate by FVA-c but does significantly uptake

of phosphate by Diaion SA10A. Uptake of phosphate by FVA-c at pH 7.63 is as high as 1.68 mmol/g, whereas phosphate uptake by Diaion SA10A at pH 6.52 is 0.78 mmol/g. As it is anticipated from Helfferich's electroselectivity (Helfferich, 1962), sulfate highly interferes with uptake of monovalent $H_2PO_4^-$ by FVA-c; phosphate is not substantially taken up by FVA-c below pH 4.26, where main anionic species is monovalent $H_2PO_4^-$. According to the electroselectivity concept, ion exchangers generally prefer counter ions with higher valence (Helfferich, 1962). Therefore, uptake of monovalent $H_2PO_4^-$ by FVA-c and Diaion SA10A is highly depressed by sulfate. With an increase in pH above pH 4.6, mole fraction of $H_2PO_4^-$ decreases but that of divalent HPO_4^{2-} increases, resulting in a decrease in the interference of sulfate. Phosphate uptake by FVA-c increases above pH 4.6 with an increase in pH up to pH 6.87, where the maximum uptake of 1.55 mmol/g is observed. With a further increase in pH, phosphate uptake decreases. Above pH 7.21 (= pKa_2), primary species is divalent HPO_4^{2-}, which cannot donate proton to free amine. In other words, the following reaction (4) does not occur because basicity of PO_4^{3-} is much higher than that of F-NH$_2$:

$$\overline{\text{F-NH}_2} + \text{HPO}_4^{2-} \rightleftharpoons \overline{(\text{F-NH}_3^+) \cdot \text{PO}_4^{3-}} \tag{4}$$

Therefore, the amount of protonated sites decreases significantly with an increase in pH above pH 7.21, because mole fraction of HPO_4^{2-} is substantially equal to 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 is 2.0 - 2.1 mmol/g and that in the presence of equimolar sulfate is 1.55 mmol/g. This means that FVA-c prefers HPO_4^{2-} to SO_4^{2-} on the contrary to the case of Diaion SA10A, which prefers clearly SO_4^{2-} to HPO_4^{2-} as estimated from comparison of **Figures 2-5(a)** and **2-5(c)**. The higher selectivity of FVA-c to phosphate over sulfate comes from the fact that basicity of HPO_4^{2-} is much higher than that of Cl$^-$ or SO_4^{2-} and hydrogen bonding interaction is possible between F-NH$_3^+$ and HPO_4^{2-} (Kimura et al., 1982b; Hosseini and Lehn, 1982).

Figure 2-5- Phosphate uptake as a function of equilibrium pH in the presence or absence of competing anions. Exchangers: FVA-c and Diaion SA10A (50 mg of each in dry state); solutions: 0.010 M phosphate solution of various pH (25 mL); Equilibration: 30 °C for 24 h. (a) in the absence of competing anion; (b) in the presence of 0.010 M sodium chloride; (c) in the presence of 0.010 M sodium sulfate.

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2.2.3.2. Column-mode study

2.2.3.2.1. Effect of flow rate

Different from the batch-mode study, FVA-f in hydrochloride form was used in the column-mode study, because the column-mode study aims at evaluation of practical performance of FVA-f in removal of phosphate from dilute concentration levels of phosphate. The outstanding characteristics of FVA are anion selectivity of non-Hofmeister type and rapid uptake of anionic species (Awual et al., 2008). 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 a 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 of pH 5.2 as feed, while it seems that even the lowest flow rate of 150 h^{-1} in this work is higher than those for granular resin packed columns (20 – 40 h^{-1}). Since the breakthrough capacity is more important than the equilibrium capacity in the column-mode removal of pollutant phosphate, the former was evaluated in this work but not the latter.

Figure 2-6 illustratively 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 through 8 in **Table 2-4**. 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 190 to 150 BV. This means that 13.3 times increase in flow rate brings only 21% decrease in the breakthrough point, indicating the excellent kinetic performances of FVA-f for uptake of phosphate different from cases of ligand exchange type adsorbents (Zhu and Jyo, 2005; Blaney et al., 2007; Genz et al., 2004; Fytianos et al., 1998). Indeed, FVA-f has the breakthrough capacity for phosphate as high as 1.14 mmol/g even at the high flow rate of 2000 h^{-1}.

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

$$\overline{F\text{-}NH_3^+ \cdot Cl^-} + H_2PO_4^- \rightleftharpoons \overline{F\text{-}NH_3^+ \cdot H_2PO_4^-} + Cl^- \tag{5}$$

$$\overline{2F\text{-}NH_3^+ \cdot Cl^-} + HPO_4^{2-} \rightleftharpoons \overline{(F\text{-}NH_3^+)_2 \cdot HPO_4^{2-}} + 2Cl^- \tag{6}$$

In addition to conventional anion exchange mechanism, the hydrogen bonding interaction occurs in uptake of phosphate as described in the preceding section. Anion exchange and hydrogen bonding interactions are much faster than ligand exchange reactions, in which ligands and/or solvent molecules initially coordinated to the central metal ion must be substituted by a target anion species (Zhu and Jyo, 2005; Blaney et al., 2007; Zhao and Sengupta, 2000; Chitrakar et al., 2006). Thus, FVA-f can take up phosphate in wide feed flow rate range from 150 through 2000 h^{-1} with high efficiency different from ligand exchange type adsorbents.

2.2.3.2.2. Elution of adsorbed phosphate and regeneration

Since phosphoric acid is weak acid with pKa_1 of 2.16, it substantially becomes non-charged species below pH 0.16. This means that phosphate adsorbed on FVA-f will be eluted by 1 M HCl according to the following reactions:

$$\overline{F\text{-}NH_3^+ \cdot H_2PO_4^-} + HCl \rightleftharpoons \overline{F\text{-}NH_3^+ \cdot Cl^-} + H_3PO_4 \tag{7}$$

$$\overline{(F\text{-}NH_3^+)_2 \cdot HPO_4^{2-}} + 2HCl \rightleftharpoons \overline{2F\text{-}NH_3^+ \cdot Cl^-} + H_3PO_4 \tag{8}$$
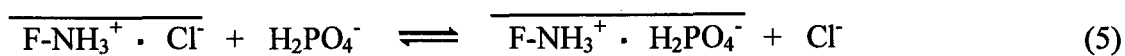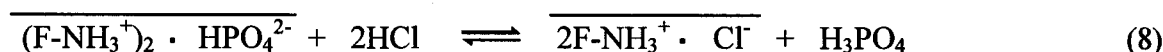
Figure 2-7 illustratively shows the typical elution profile of phosphate in elution operation with 1 M HCl at a flow rate of 10 h^{-1}; phosphate adsorbed on the FVA-f packed column was quantitatively eluted with 16 BV of 1 M HCl as listed in **Tables 2-4, 2-5**, and **2-6**. From equations (7) and (8), it is clear that this elution procedure simultaneously regenerate FVA-f into hydrochloride form. After regeneration FVA-f in hydrochloride form, the column was rinsed with water to remove free hydrochloric acid as condition in **Figure 2-8**. Therefore, FVA-f was able to use to remove phosphate from water in many cycles.

2.2.3.2.3. Effect of phosphate concentration in 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 of pH 5.2

containing phosphate from 0.071 to 1.62 mM. Here, the flow rate of feeds was fixed at 1000 h^{-1}. Results are given in **Table 2-4** (entry nos. 5, 6, 9 – 14) and **Figure 2-9**, which shows breakthrough points and capacities as a function of C_0. With a decrease in C_0, the breakthrough point markedly increased but the breakthrough capacity decreased slightly. **Figure 2-9** clearly shows that the decrease in the breakthrough capacity down to 0.40 mM in C_0 is 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 C_0, it depends on the definition of the breakthrough point. For instance, the breakthrough point in this work is designated as the feed volume up to C = 0.01 C_0. Therefore, the lower the concentration of phosphate in the feed (C_0), the stricter the criterion for determining the breakthrough point, leading to the smaller breakthrough capacity. This probably is the reason for the breakthrough capacity profiles on C_0 in **Figure 2-9**.

2.2.3.2.4. Rapid removal of trace phosphate

When huge volume of water is contaminated with phosphate of ppm or sub-ppm levels as P, kinetically excellent adsorbents are very advantageous to rapid removal of phosphate. Then, phosphate removal was tested supplying two feeds containing 0.035 mM (1.1 ppm as P) or 0.021 mM (0.65 ppm as P) phosphate to the column at a flow rate of 2500 h^{-1}; namely, supplying 6.00 L of each phosphate feed to the column (fiber bed of 2.4 mL) for 1 h. **Figure 2-10** shows breakthrough profiles of phosphate in these phosphate removal operations. The detailed experimental conditions and numerical results are given in **Table 2-4** (entry nos. 15 – 18). In case of 0.035 mM of phosphate feed, the breakthrough point was ca. 4370 BV and the breakthrough capacity was 0.74 mmol/g. In case of the alternative 0.021 mM phosphate feed, the breakthrough point was ca. 6870 BV and its breakthrough capacity 0.67 mmol/g. This means that 16.5 L of water containing phosphate at 0.65 ppm as P can be purified down to less than 0.0065 ppm as P, which is lower than the upper limit recommended by Florida Everglades Forever Act (Florida Everglades Forever Act, 1994).

Table 2-4- Column-mode uptake of phosphate by FVA-f under different feed flow rates and feed concentrations

Entry no.	Feed solution pH	Feed flow rate (h⁻¹ in SV)	Feed C$_0$ of phosphate (mM)	Feed volume (BV)	Breakthrough point (BV)	Breakthrough capacity (mmol/g)	Phosphate adsorbed (mmol/g)	Phosphate eluted (mmol/g)	Recovery (%)
1	5.26	150	1.61	400	192	1.48	2.51	2.40	95.6
2	5.26	150	1.61	400	189	1.46	2.50	2.34	93.6
3	5.31	500	1.62	400	179	1.40	2.34	2.36	101
4	5.31	500	1.62	400	172	1.34	2.32	2.24	96.5
5	5.34	1000	1.62	400	160	1.25	2.22	2.20	99.1
6	5.34	1000	1.62	400	157	1.22	2.22	2.28	102
7	5.33	2000	1.57	400	149	1.12	2.03	1.99	98.0
8	5.33	2000	1.57	400	152	1.15	2.00	2.02	101
9	5.27	1000	0.796	833	292	1.12	2.41	2.42	100
10	5.27	1000	0.796	833	296	1.13	2.40	2.30	95.8
11	5.25	1000	0.402	1667	556	1.07	2.34	2.26	96.6
12	5.26	1000	0.402	1667	546	1.05	2.36	2.36	100
13	5.28	1000	0.072	5208	2448	0.849	1.57	1.64	104
14	5.29	1000	0.071	5208	2466	0.846	1.54	1.70	110
15	7.01	2500	0.035	8333	4350	0.740	1.26	1.27	101
16	7.02	2500	0.035	8333	4390	0.742	1.25	1.28	102
17	7.02	2500	0.020	11667	6815	0.668	1.06	1.04	97.2
18	6.98	2500	0.021	11667	6925	0.685	1.07	1.09	101

Wet fibers bed: 2.4 mL.

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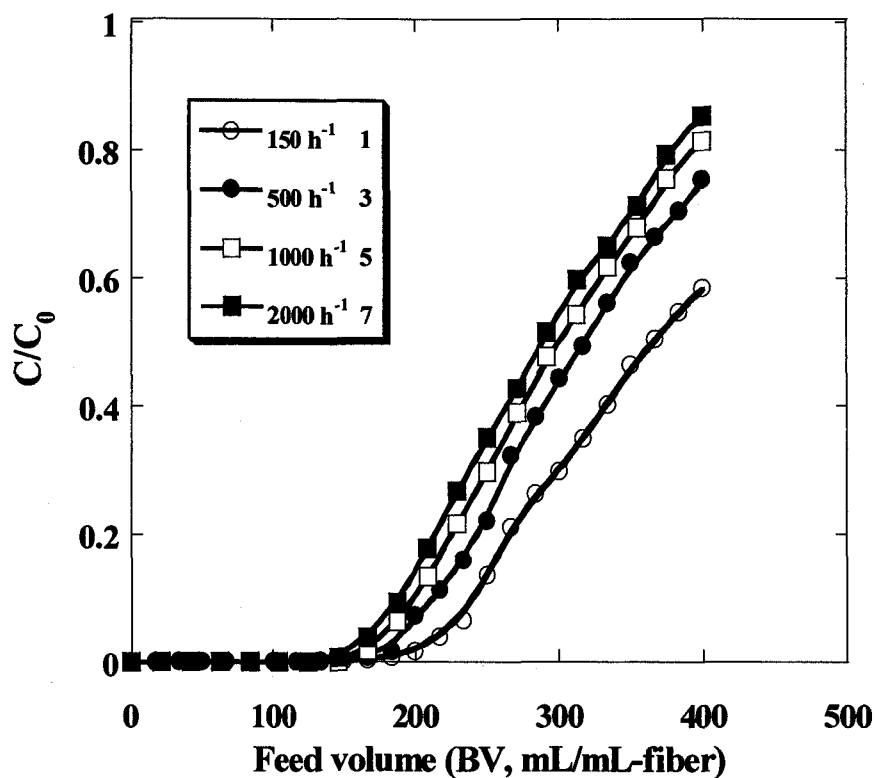
Figure 2-6- Breakthrough profiles of phosphate adsorption by FVA-f under different flow rates of feed. Figure on each profile corresponds to entry nos. 1, 3, 5, and 7 in Table 2-4. For detailed conditions and numerical results refer to entry nos. 1, 3, 5 and 7 in Table 2-4.
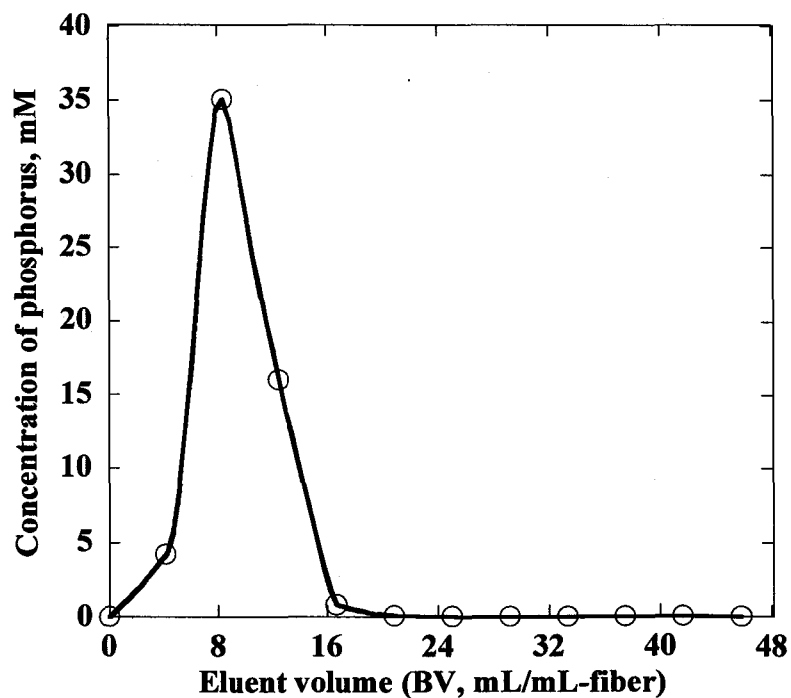
Figure 2-7- Elution of phosphate adsorbed on FVA-f column with 1 M HCl at a flow rate of 10 h^{-1}. For detailed conditions and numerical data, refer to entry no. 18 in Table 2-4.
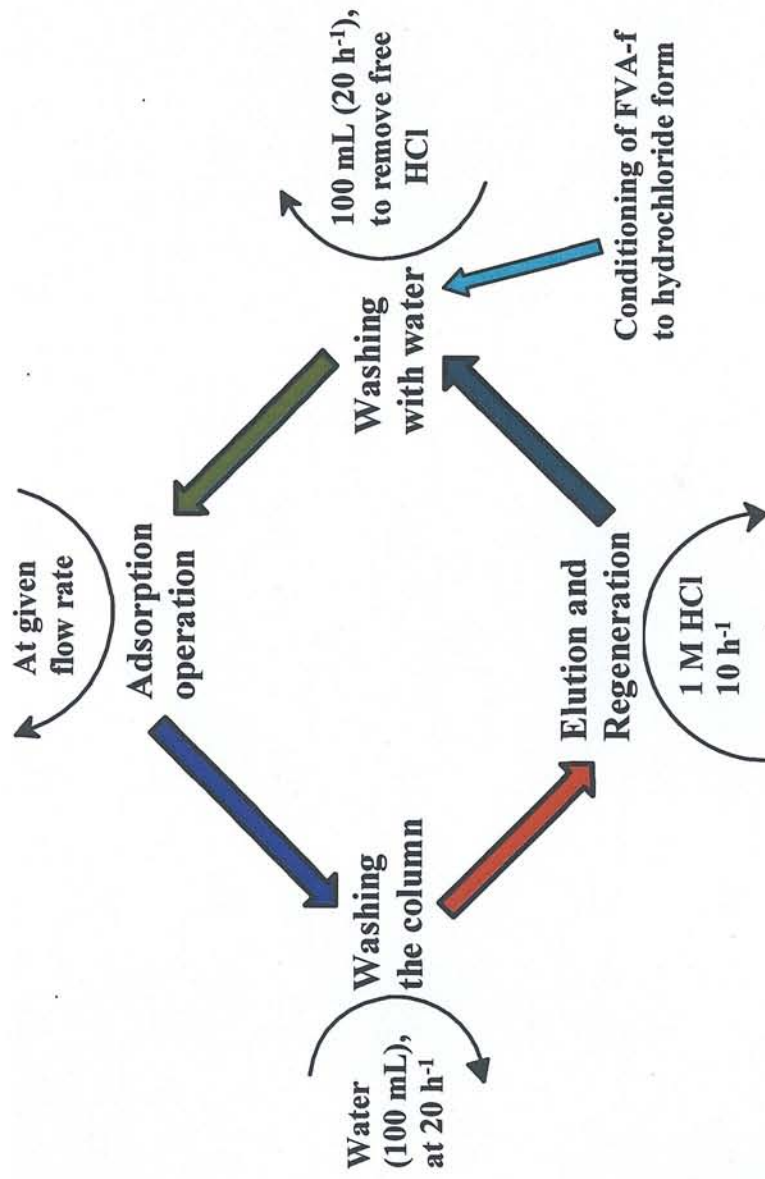
Figure 2-8- Schematic illustration of repeated uses of FVA-f fiber packed column in a cycle of adsorption-elution & regeneration

50
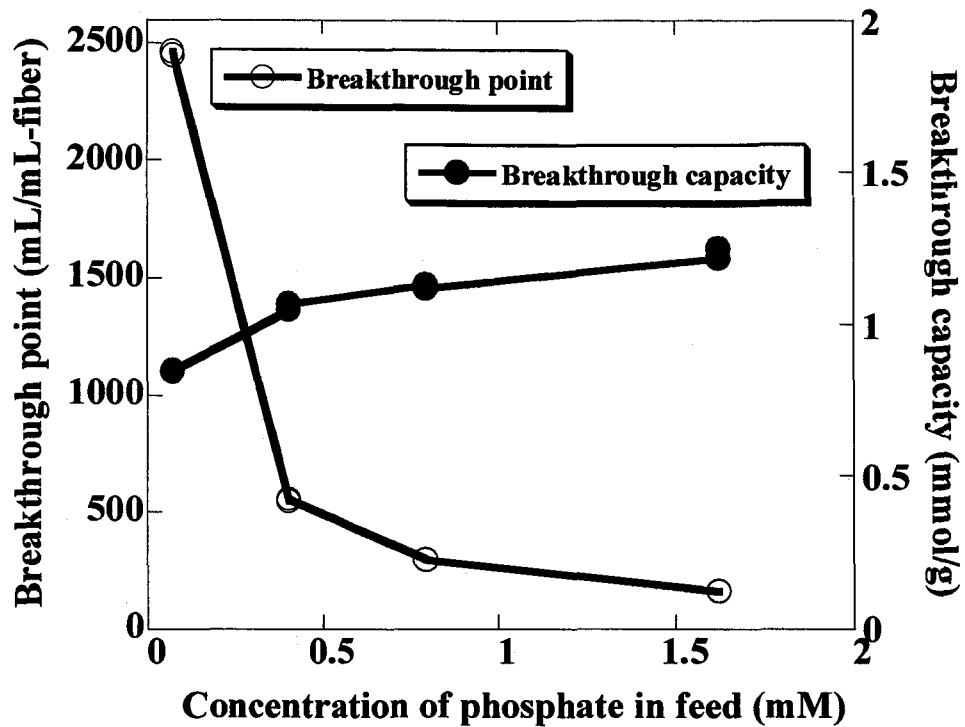
Figure 2-9- Effect of feed concentration on phosphate uptake by FVA-f. For detailed conditions and results refer to entry nos. 5, 6 and 9-14 in Table 2-4.
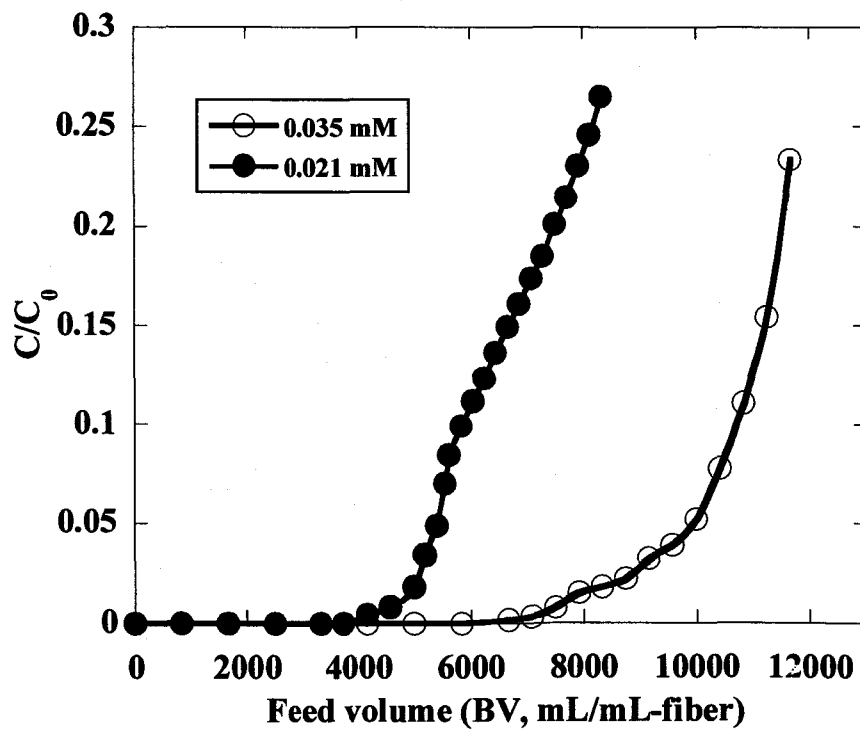
Figure 2-10- Phosphate uptake by FVA-f from feeds containing trace levels of phosphate at a feed flow rate of 2500 h^{-1}. Figure on each profile corresponds to entry nos. 15 and 17 in Table 2-4. For detailed conditions and results refer to entry nos. 15 and 17 in Table 2-4.

2.2.3.2.5. Effect of co-existing anions

Because main anions in river and lake waters are chloride and sulfate, their effect on uptake of phosphate was tested using feeds containing chloride or sulfate as competing anion at equimolar or 5 times molar of phosphate. **Figure 2-11** shows the breakthrough curves of phosphate, and detailed experimental conditions and numerical results are summarized in **Table 2-5**.

Phosphate uptake was not strongly adversely affected in the presence of chloride; breakthrough capacities for phosphate in the presence of equimolar and 5 times molar chloride are 0.994 and 0.888 mmol/g, respectively. These values are comparable to the breakthrough capacity for phosphate (1.06 mmol/g) in the absence of competing anion under the same flow rate and C_0 (entry nos. 11 and 12 in **Table 2-4**). Total uptake of phosphate was also not highly affected in the presence of chloride as listed in **Table 2-5** (entry nos. 19, 20, 23, 24); values of the total uptake are 2.29 and 2.14 mmol/g in the presence of equimolar and 5 times molar chloride, respectively, and are close to the control values of 2.35 mmol/g (entry nos. 11 and 12 in **Table 2-4**).

In the presence of equimolar sulfate, on the other hand, breakthrough capacity for phosphate (0.862 mmol/g) was not so markedly affected by sulfate but the total uptake (1.72 mmol/g) is significantly less than the control one (entry nos. 21 and 22 in **Table 2-5**). In the presence of 5 times molar sulfate, interference by sulfate became more marked; breakthrough capacity for phosphate and total uptake of phosphate are reduced to 0.492 and 1.35 mmol/g, respectively (entry nos. 25 and 26 in **Table 2-5**). However, these values are much greater than one-fifths of respective control values 0.212 and 0.47 mmol/g, indicating that FVA-f prefer phosphate to sulfate, different from column-mode uptake of phosphate in the presence of sulfate by strong-base anion exchange resins (Blaney et al., 2007; Zhao and Sengupta, 2000). In metal loaded ligand exchange type resins, phosphate uptake was not interfered with common anions but they cannot take up effectively phosphate at high flow rates much higher than 100 h^{-1} (Zhu and Jyo, 2005; Blaney et al., 2007).

2.2.3.2.6. Competitive uptake of arsenate and phosphate

Arsenic and phosphoric acids have very similar properties. Of interest is therefore the competitive uptake of arsenate and phosphate by FVA-f, because we reported that FVA-f selectively takes up arsenate from water at high feed flow rate (Awual et al., 2008). Then, the competitive uptake of arsenate and phosphate by FVA-f was tested supplying a feed containing equimolar of both anions (0.33 mM of each) to the FVA-f column at a flow rate of 150 h^{-1}. As judged from data in **Table 2-4**, the highest breakthrough capacity was observed at the flow rate of 150 h^{-1}, and then this flow rate was selected to observe more clearly the difference in breakthrough capacities for both anions. **Figure 2-12** shows breakthrough profiles of both anions. Conditions and numerical results are given in **Table 2-6**. The breakthrough point of arsenate (317 BV) was found to be smaller than that of phosphate (384 BV), leading to respective breakthrough capacities of 0.498 and 0.606 mmol/g. After the breakthrough point of arsenate, the arsenate concentration in the effluent more sharply increased than that of phosphate. Then, total uptake of arsenate (0.920 mmol/g) was also less than that of phosphate (1.19 mmol/g). These results mean that FVA-f prefers phosphate to arsenate. Although both divalent arsenate and phosphate anions can form hydrogen bonds with F-NH$_3^+$, basicity of arsenate is close to that of phosphate since both parent acids, phosphoric and arsenic acids, have very close values of pKa$_1$, pKa$_2$, and pKa$_3$. Then, the significant difference does not exist in strength of the hydrogen bond of each anion with F-NH$_3^+$ between arsenate and phosphate. On the other hand, meaningful difference can be seen between sizes of both anions. In HAsO$_4^{2-}$, lengths of three equivalent As-O bonds are 0.1654 through 0.1671 nm and As-O bond length in As-OH is 0.1742 nm (Schwendtner and Kolitsch, 2004). Similarly, lengths of three equivalent P-O bonds are 0.1510 through 0.1524 nm and P-O bond length in P-OH is 0.1551 through 0.1564 nm (Troup and Clearfield, 1977). This means that crystallographic size of divalent phosphate anion is smaller than that of divalent arsenate anion. Then, it is estimated that Coulombic interaction between phosphate and positive sites is greater than that in case of arsenate, resulting in the stronger interaction of phosphate with positive site than arsenate. Therefore, phosphate might overcome arsenate in competition for overall binding with positive sites.

Table 2-5- 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 (%)
	solution pH	C_0 of phosphate (mM)	NaCl (mM)	Na_2SO_4 (mM)					
19	5.24	0.401	0.4		518	0.997	2.25	2.24	99.6
20	5.24	0.401	0.4		515	0.991	2.23	2.34	105
21	5.27	0.403		0.4	448	0.866	1.74	1.66	95.4
22	5.27	0.403		0.4	444	0.858	1.70	1.76	103
23	5.29	0.397	2.0		468	0.893	2.16	2.14	99.1
24	5.29	0.397	2.0		462	0.882	2.12	2.22	105
25	7.02	0.402		2.0	260	0.503	1.49	1.42	95.3
26	7.02	0.402		2.0	249	0.481	1.21	1.13	93.3

Wet fibers bed: 2.4 mL, flow rate of feed: 1000 h^{-1}, volume of feed: 1667 BV.

Table 2-6- 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
27	380	315	0.599	0.496	1.18	0.903	1.20	0.888	102	98.3
28	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}.
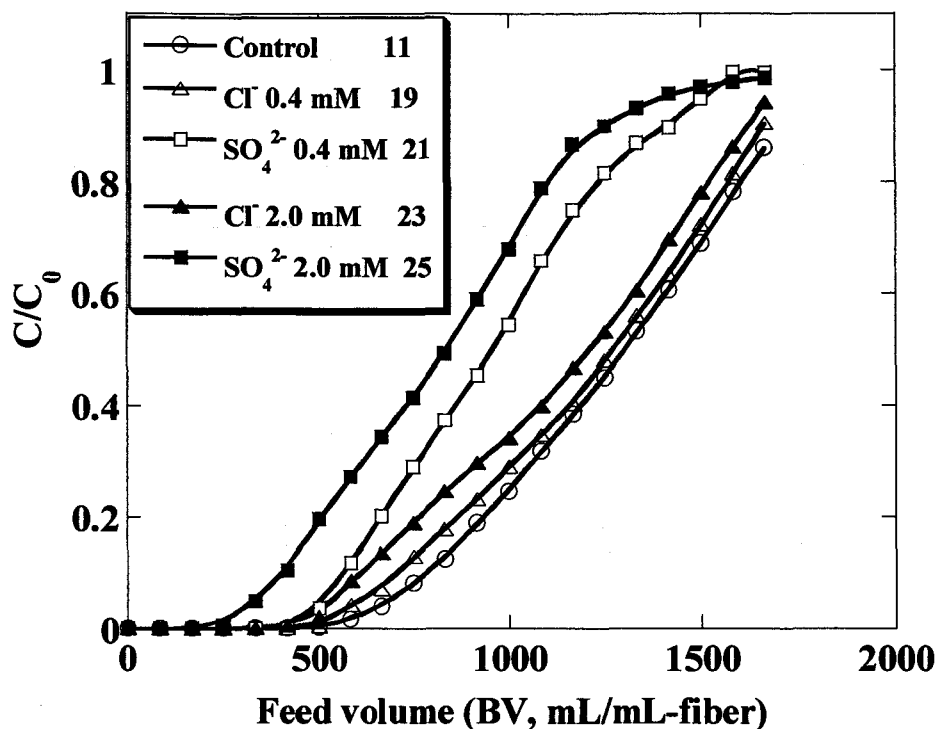
Figure 2-11- Effect of competing anions on phosphate uptake by FVA-f. Figure on each profile corresponds to entry no. 11 in Table 2-4 and entry nos. 19, 21, 23 and 25 in Table 2-5. For detailed conditions and numerical results refer to entry no. 11 in Table 2-4 and entry nos. 19, 21, 23 and 25 in Table 2-5.
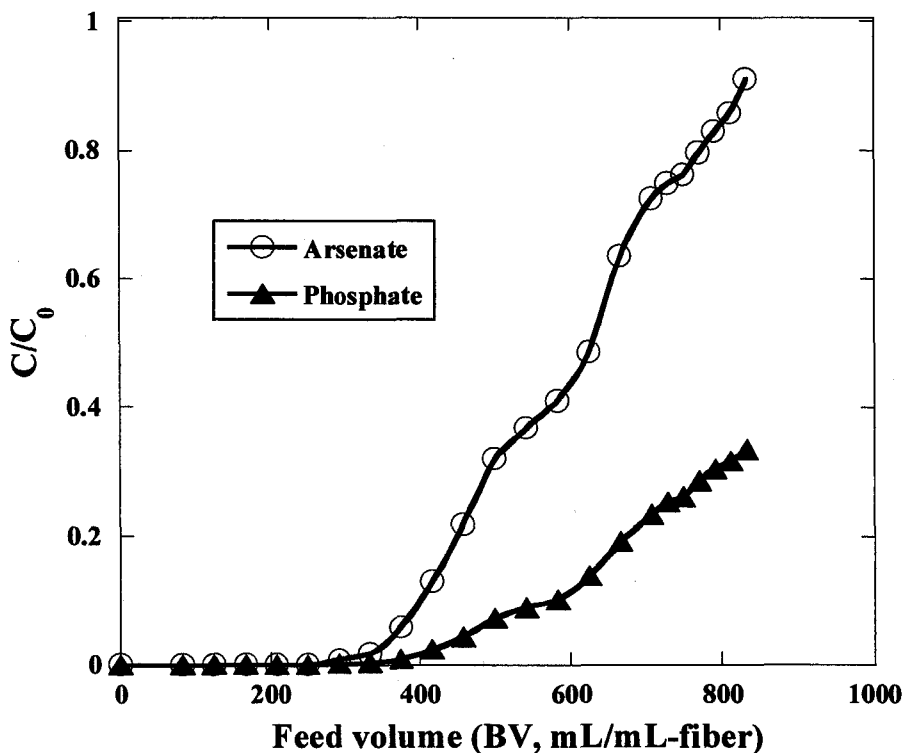
Figure 2-12- Competitive uptake of arsenate and phosphate by FVA-f. Feed: a solution containing both arsenate and phosphate at 0.33 mM of each, pH 7.02, flow rate 150 h^{-1}. For detailed conditions and numerical results refer to entry no. 27 in Table 2-6.

It is very important to use the adsorbent without deterioration in its performances during many adsorption-elution-regeneration cycles for a long while. All results in the column-mode study were obtained using the same column without replacement of FVA-f for four months.

2.2.4. Conclusions

The fibrous weak-base anion exchange adsorbent FVA has high selectively to phosphate. Batch-mode study clarified that the FVA-c prefers phosphate to chloride and sulfate in neutral pH regions, different from strong-base anion exchange resin having crosslinked poly(styrene) matrices, such as Diaion SA10A, which prefers chloride and sulfate to phosphate. Because FVA was able to make hydrogen bonding with divalent phosphate but not with chloride or sulfate. Moreover, equilibrium capacity of FVA-c for phosphate is much higher than that of the strong-base resin of Diaion SA10A. Therefore, FVA exhibits non-Hofmiester anion selectivity sequence of phosphate > arsenate > chloride > sulfate. Column-mode study clarified that the protonated FVA-f was able to take up phosphate very rapidly from the feed containing phosphate in different concentrations. The breakthrough capacities for phosphate are not strongly affected of feed flow rate from 150 to 2000 h^{-1} and it decreased from 1.47 to 1.13 mmol/g, respectively. Therefore, FVA-f shows excellent kinetic performances to take up phosphate at high feed flow rate. According to high the breakthrough capacity and adsorption rate, trace concentrations of feed solutions containing 0.65 mg/L and 1.1 mg/L of phosphorus at pH ca. 7.0 were supplied to the column at feed flow rate of 2500 h^{-1}. Under these conditions, breakthrough points are 6870 and 4370 bed volumes, leading to relevant breakthrough capacities of 0.676 and 0.741 mmol/g, respectively. Phosphate uptake was not strongly interfered with chloride and sulfates even the concentration ratio of phosphate and anions were equimolar and fivefold molar in column-mode. The adsorbed phosphate was quantitatively eluted with 1 M hydrochloric acid and the FVA-f was regenerated simultaneously into hydrochloride form for the next adsorption operation after rinsing with water. Therefore, the fibrous anion exchanger is able to use repeatedly without any deterioration for long term to remove phosphate from water at high feed flow rate.

Chapter-3

3.1. Removal of trace arsenate and phosphate from water by Zr(IV) loaded monophosphonic acid resin

3.1.1. Introduction

Some toxic elements even at trace amount are adversely affected on human health which demands to invent for new separation processes to purify the drinking water. It is prominent that arsenate and phosphate are hazardous anions for human being as well as environment. Arsenic is one of the most abundant elements in the Earth's crust. Millions of people in the world are adversely affected by arsenic contaminated water (Chowdhury et al., 2000; Brown and Ross, 2002; Choong et al., 2007; Kinniburgh and Smedley, 2001). A new maximum contamination level is permitting the presence of low arsenic in drinking at 10 µg/L due to its high toxicity (WHO, 1993). On the other hand, low concentration of phosphorus in wastewater is responsible for eutrophication. Recently, a new mandate has been established for phosphorus reduction in wastewater effluent at 10 µg/L (Florida Everglades Forever Act, 1994).

Many researchers devoted their effort and invented new techniques to remove arsenate and phosphate from water to safe the human being as well as natural environment. Recently proposed methods are precipitation, activated alumina, adsorption by suitable adsorbents, membrane filtration and biological removal (Mino et al., 1998; Ahmad et al., 2005; Choong et al., 2007; Awual et al., 2008; Kargi et al., 2005). To this date, metal loaded ligand exchange adsorbents are attractive to remove arsenate and phosphate from water due to its high selectivity even the existing common anions concentration were more higher than those selected anions. The number of metal ions such as Fe(III), Al(III), La(III) and Zr(IV) are immobilized on chelating resins or fibers to removed hazardous anions (Matsunaga et al., 1996; Katsoyiannis and Zouboulis, 2002; Meng et al., 2002; Kabayama et al., 2003; Gu et al., 2005; Zhu and Jyo, 2005). Several researchers developed the metal oxide or hydroxide loaded adsorbents for water purification (Tokunaga et al., 1997; Cumbal and Sengupta, 2005; Blaney et al., 2007). These are promising to removed arsenate and phosphate from water in the presence of high concentration common anions.

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This study aims for (1) high uptake capacity both for arsenate and phosphate, (2) high selectivity toward target anions in the presence of competing anions and (3) the reusability.

In this work, we report on uptake of arsenate and phosphate from water by Zr(IV) loaded monophosphonic acid resin (MPR). The MPR is a bifunctional cation exchange resin having both phosphonic and sulfonic acid groups (**Scheme 3-1**) and can strongly take up Zr(IV) through strong complexation with phosphonate. Experiments were carried out to investigate the effect of feed solution pH and competing anions on uptake of the target anions.

3.1.2. Experimental

3.1.2.1. Materials

Monophosphinic acid resin was kindly provided by Muromachi Chemical Co., Omuta, Japan. $Zr(SO_4)_2$ was purchased from Wako Pure Chemical Industries Co., Osaka, Japan. Ultra-pure water (Milli-Q, Academic-A10, Nippon Millipore Co., Tokyo, Japan) was used throughout. Arsenate and phosphate solutions were prepared using sodium dihydrogenarsenate and disodium hydrogenphosphate. All chemicals reagents were used of guaranteed grade unless otherwise specified. The acid capacity, phosphorus and sulfur contents were determined by reported methods (Maeda and Egawa, 1984). The acid capacity of MPR is 8.6 meq/g and its phosphorus and sulfur contents were 3.4 and 1.6 mmol/g, respectively. Its chemical structure is shown in **Scheme 3-1.**
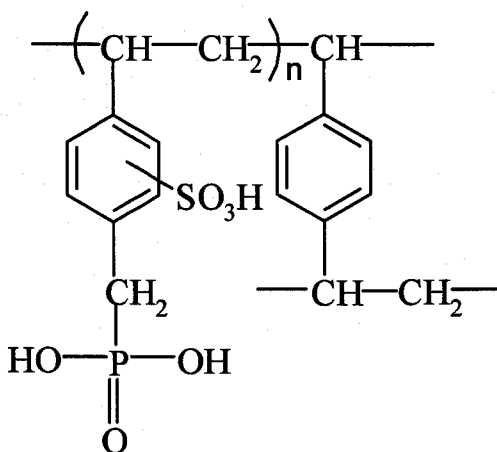
Scheme 3-1- Monophosphonic acid resin (MPR)

3.1.2.2. Preparation of Zr(IV) loaded column

Zr(IV) was loaded onto MPR by column-mode method. Hydrogen form of MPR (wet volume 2.0 mL) was taken into polyethylene column (inner diameter 1.3 cm). The Zr(IV) loading solution (0.01 M Zr(IV) in 0.5 M H_2SO_4) was fed to the column at a flow rate of 3 h^{-1} in space velocity (SV) until the column was nearly saturated with Zr(IV). After successive washing column with water, 0.2 M NaOH, water, and 0.5 M H_2SO_4, the Zr(IV) loading solution was supplied to the column again. These procedures were repeated. All column effluents were collected on a fraction collector and the concentration of Zr(IV) in each fraction was determined by ICP-AES. The total amount of immobilized Zr(IV) onto MPR was calculated by subtracting amounts of Zr(IV) passed through the column from the total amount of Zr(IV) supplied to the column.

3.1.2.3. Column-mode adsorption, elution and regeneration

Arsenate and phosphate feed solutions were prepared by dissolving $Na_2HAsO_4 \cdot 7H_2O$ and $NaH_2PO_4 \cdot 2H_2O$ in water, respectively. The pH of feed solutions was adjusted by adding dilute sulfuric acid and sodium hydroxide solution when needed. Before adsorption operation, the Zr(IV) loaded column was conditioned to be the same pH as that of feed solutions. All feed solutions were fed to the column at a given flow rate. After adsorption operation, the column was washed with water (30 mL) and adsorbed arsenate and phosphate was eluted with 0.1 M sodium hydroxide solution at a flow rate of 3 h^{-1} in SV. After washing the column with water to be neutral, 0.5 M sulfuric acid (10 bed volumes, BV) was fed to column for regeneration. In the regeneration operation, little amount of Zr(IV) was leaked. For this reason, Zr(IV) solution(5 BV) in 0.5 M sulfuric acid media was fed to the column. Then the Zr(IV) loaded column was ready for next adsorption operation after washing with water. All column effluents were collected on a fraction collector and phosphorus and zirconium concentrations in each fraction were determined by ICP-AES. Arsenic concentration in each fraction was determined by arsine hydride generation method. Arsenate and phosphate adsorption on Zr(IV) loaded column were calculated from the breakthrough profiles in each run. Here, the breakthrough point was defined as the volume of feed supplied to the column up to $C/C_0 = 0.01$, where C_0 and C stand for the arsenic concentrations in feeds and in column effluents, respectively. In the

case of phosphate adsorption, the breakthrough point was defined by the feed volume up to C of P = 10 μg/L. Supplied solutions to the columns in adsorption-elution-regeneration operations are expressed by unit of bed volumes (BV), which is defined by the ratio of $V_{supplied}/V_{bed}$; here $V_{supplied}$ is volumes of solutions in mL. Flow rate is calculated by the ratio of F/V_{bed}; here F is flow rates of solutions in mL/h and V_{bed} is a volume of the resin bed in the reference state (2.0 mL).

3.1.3. Results and discussion

3.1.3.1. Loading of Zr(IV) onto resin

In good ligand exchanger, loaded metal ions should be retained on chelating resin or fiber without any leakage in wide pH range. Zr(IV) binds so strongly that it can be immobilized on chelating resin even in strongly acidic media (Zhu and Jyo, 2001b). Then, Zr(IV) loaded column would be useful as a ligand exchanger to remove arsenate and phosphate. The amount of immobilized Zr(IV) on MPR in the first run was 0.39 mmol/mL. The value for pKa_1 of phosphonic acid is 2 – 3. The dissociation of phosphonic acid group will be depressed below pH 2 - 3, resulting incomplete swelling of phosphonate groups. Then the loading procedures of Zr(IV) on MPR were repeated 11 times to increase the total amount of immobilization. The total amount of Zr(IV) on MPR after 11 runs increased up to 0.99 mmol/mL. The stability of loaded Zr(IV) on MPR was investigated by supplying 0.5 M sulfuric acid and 0.2 M sodium hydroxide solutions to the column. A little amount of Zr(IV) was observed in 0.5 M sulfuric acid flowed out from the column but was negligibly low compared to the total immobilized of Zr(IV) on MPR.

3.1.3.2. Effect of pH of feeds on adsorption

Figure 3-1 shows effect of pH of feeds in column-mode uptake of arsenates by Zr(IV) loaded MPR. Here, the concentration of arsenate in feeds was 0.020 mM and flow rate of feed was 10 h^{-1}. The proposed ligand exchanger works well in wide pH ranges from 2 to 7. Breakthrough points for arsenate decreased from 245 to 180 BV with an increase in pH of feeds from 2 to 7. Breakthrough capacities were from 0.0035 to 0.0048 mmol/mL of

wet adsorbent as shown in **Table 3-1** (entry nos. 1 through 10), which lists detailed conditions and numerical results. These results imply that the breakthrough points decrease with increasing the pH of feed. Zr(IV) is a hard Lewis acid, and shows the highest affinity to OH⁻ (Schwarzenbach and Schellenberg, 1968; Pearson, 1968). With an increase in pH, hydroxide binds with Zr(IV) in preference to arsenate species. In other words, lower pH is preferable for uptake of arsenate anions (Zhu and Jyo, 2001a; Katsoyiannis and Zouboulis, 2002; Gu et al., 2005). In acidic pH region up to 2, no measurable Zr(IV) was found in column effluents during adsorption operation.

3.1.3.3. Effect of anions on arsenate adsorption

Groundwater contains several kinds of anions such as chloride and sulfate. Therefore, effect of these anions on arsenate uptake was tested using feeds listed in **Table 3-1** (entry nos. 11 through 14). **Figure 3-2** shows the effects of anions on arsenate adsorption. Chloride and sulfate did not interfere with uptake of arsenate but slightly increased the breakthrough capacities and total uptake as shown in **Table 3-1**. Several researchers also found the same trends on arsenate adsorption by metal ion loaded adsorbent (Zhu and Jyo, 2001a). This comes from the enhancement of adsorption of arsenate by co-ion (sodium ion) because Zr(IV) so strongly take up arsenate that sodium ion must invade into exchanger phase to keep electroneutrality through so called Donnan invasion mechanism (Helfferich, 1962).

Table 3-1- Detailed conditions and results on column-mode uptake of arsenate by Zr(IV) loaded monophosphonic acid resin (MPR)

Entry no.	Feed solution pH	Feed C_0 of arsenate (mM)	Breakthrough point (BV)	Breakthrough capacity (mmol/mL)	Arsenate adsorbed (mmol/mL)	Arsenate eluted (mmol/mL)	NaCl (mM)	Na_2SO_4 (mM)	Recovery (%)
1	2.01	0.020	245	0.0049	0.0056	0.0055			98.2
2	2.01	0.020	240	0.0048	0.0055	0.0055			100
3	3.03	0.020	234	0.0047	0.0055	0.0057			103
4	3.03	0.020	231	0.0047	0.0055	0.0055			100
5	4.01	0.020	220	0.0044	0.0054	0.0053			98.1
6	4.01	0.020	217	0.0041	0.0054	0.0055			102
7	5.62	0.019	203	0.0040	0.0052	0.0051			98.1
8	5.62	0.019	200	0.0039	0.0052	0.0048			92.3
9	6.97	0.019	186	0.0035	0.0047	0.0046			97.8
10	6.97	0.019	180	0.0035	0.0048	0.0047			97.9
11	3.01	0.021	253	0.0051	0.0056	0.0058	0.20		103
12	3.01	0.021	252	0.0051	0.0056	0.0057	0.20		102
13	3.02	0.021	255	0.0054	0.0059	0.060		0.21	102
14	3.02	0.021	261	0.0056	0.0059	0.0058		0.21	98.3

Resin wet volume: 2.0 mL, volume of feed: 275 bed volumes, feed flow rate: 10 h^{-1} in SV.
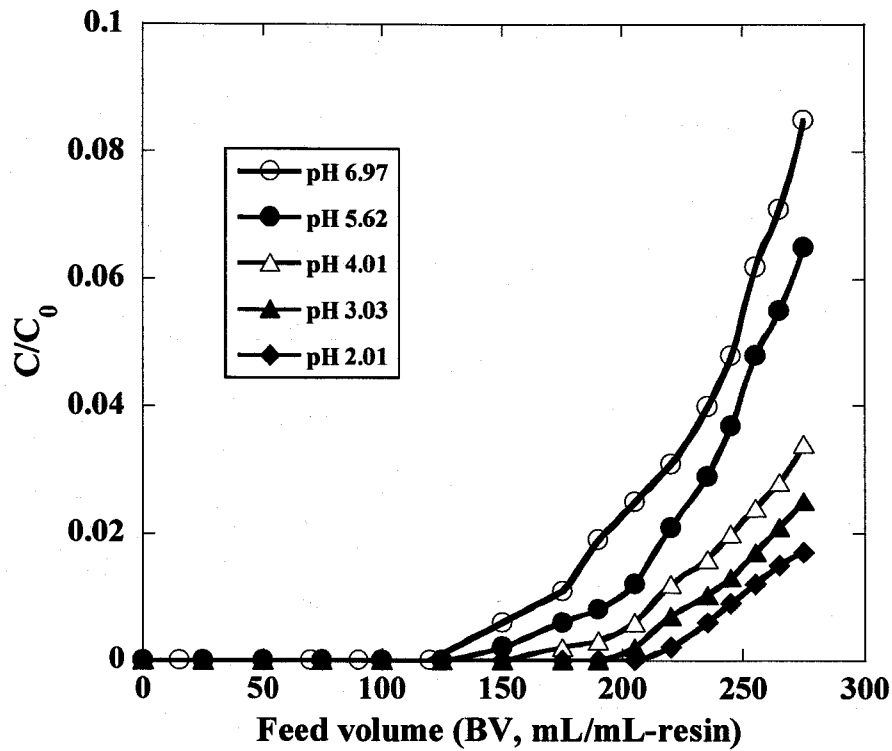
Figure 3-1- Effect of pH on arsenate uptake by Zr(IV) loaded MPR. Figure after pH values in inset corresponds to entry nos. 1, 3, 5, 7, and 9 in Table 3-1. For detailed conditions and numerical results refer to entry nos. 1, 3, 5, 7, and 9 in Table 3-1.
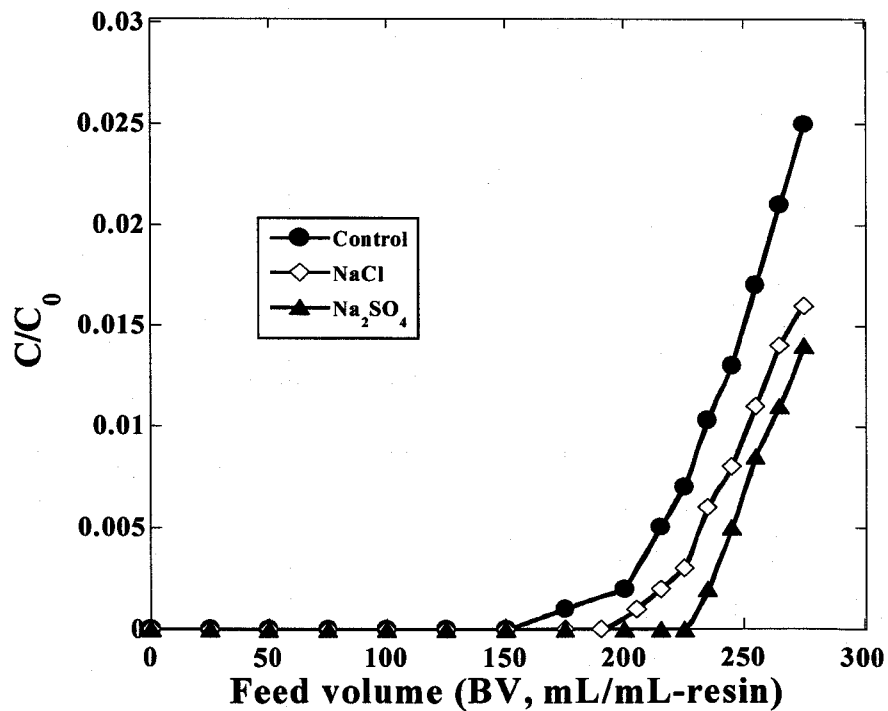
Figure 3-2- Effect of competing anions on arsenate uptake by Zr(IV) loaded MPR. Figure after explanation of anions in inset corresponds to entry nos. 4, 12, and 14 in Table 3-1. For detailed conditions and numerical results refer to entry nos. 4, 12, and 14 in Table 3-1.

3.1.3.4. Phosphate adsorption in the presence of three competing anions

Because phosphoric acid has chemical properties very close to those of arsenate, it is expected that Zr(IV) loaded MPR will selectively take up phosphate species. Then, column-mode uptake of phosphate was also examined using feeds containing phosphate, chloride, bicarbonate, and sulfate.

Figure 3-3 shows the breakthrough profiles of phosphate adsorption in two different concentrations of phosphate feed solutions. **Table 3-2** lists detailed experimental conditions and numerical results. As shown in **Table 3-2**, breakthrough points of phosphate increased with a decrease in phosphate concentrations in influent, whereas breakthrough capacities are not so markedly affected by ionic compositions of influents. Therefore, Zr(IV) loaded adsorbent worked very well to adsorb phosphate at neutral pH area, suggesting that Zr(IV) loaded adsorbent is highly selective to phosphate over chloride, bicarbonate and sulfate. Metal and metal oxide or hydroxide loaded adsorbent have no adverse effect due to high concentration of existing anions (Zhu and Jyo, 2005; Blaney et al., 2007). On the other hand, phosphate removal by commercially granular strong and weak base resin except for a few special resins was strongly affected in the presence of competing chloride, bicarbonate and sulfate. Interestingly, the Zr(IV) loaded adsorbent kept the same capability in adsorption of phosphate after the elution and regeneration operations, indicating that reusability of Zr(IV) loaded MPR without any noticeable change.

3.1.3.5. Elution of adsorbed arsenate and phosphate

The adsorbed arsenate and phosphate was able to be quantitatively eluted with aqueous sodium hydroxide as shown in **Figure 3-4**. Hydroxide is the hardest Lewis base and it is effective to elute adsorbed arsenate and phosphate as described elsewhere. During elution operation, no measurable Zr(IV) was found in the column effluents. After elution operation, the column was regenerated by 0.5 M sulfuric acid. During regeneration operation, a little amount of Zr(IV) was leaked out and the amount not more than 0.0044 mmol/mL-R. Therefore, 0.01 M of Zr(IV) solution (5 BV) was fed to the column to recover the leakage amount of immobilized Zr(IV) onto the column. Then, the column was washed with water to adjust the pH for next adsorption-elution-regeneration operations.

Table 3-2- Detailed conditions and results on column-mode uptake of phosphate by Zr(IV) loaded monophosphonic acid resin in the presence of three competing anions

Entry no.	Feed solution pH	Feed C_0 of phosphate (mM)	Feed volume (BV)	Breakthrough point (BV)	Breakthrough capacity (mmol/mL)	Phosphate adsorbed (mmol/mL)	Phosphate eluted (mmol/mL)	Recovery (%)
15	6.97	0.043	500	178	0.0077	0.0126	0.0118	93.6
16	6.97	0.043	500	190	0.0082	0.0125	0.0121	96.8
17	6.95	0.018	500	372	0.0065	0.0083	0.0086	104

Resin wet volume: 2.0 mL; feed flow rate: 30 h^{-1} in SV; competing anions: Cl^- (0.28 mM), HCO_3^- (0.24 mM) and SO_4^{2-} (0.21 mM)
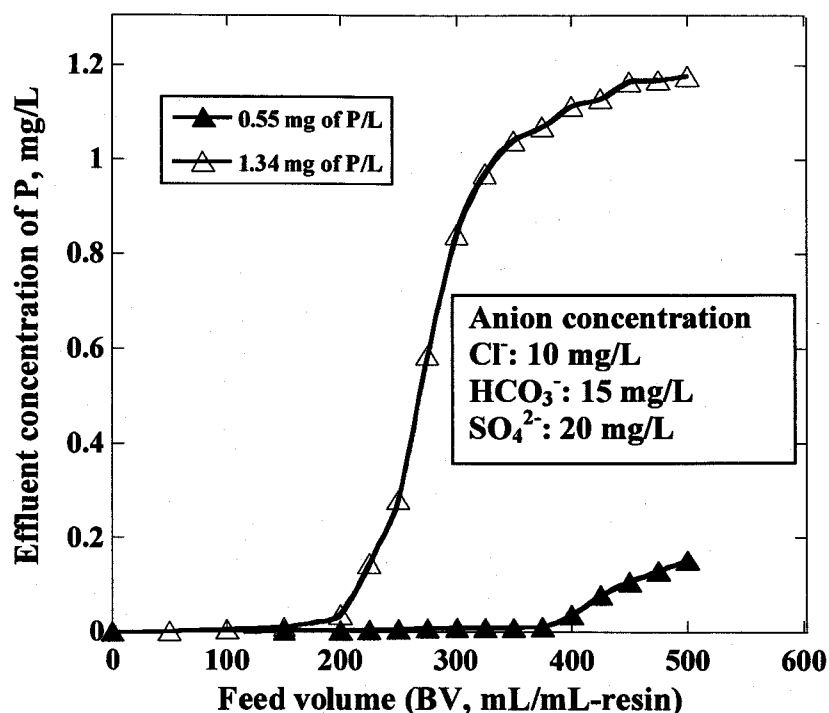
Figure 3-3- Phosphate adsorption by Zr(IV) loaded MPR in neutral pH. Figure after concentration value in inset corresponds to entry nos. 15 and 17 in Table 3-2. For detailed conditions and numerical results refer to entry nos. 15 and 17 in Table 3-2.
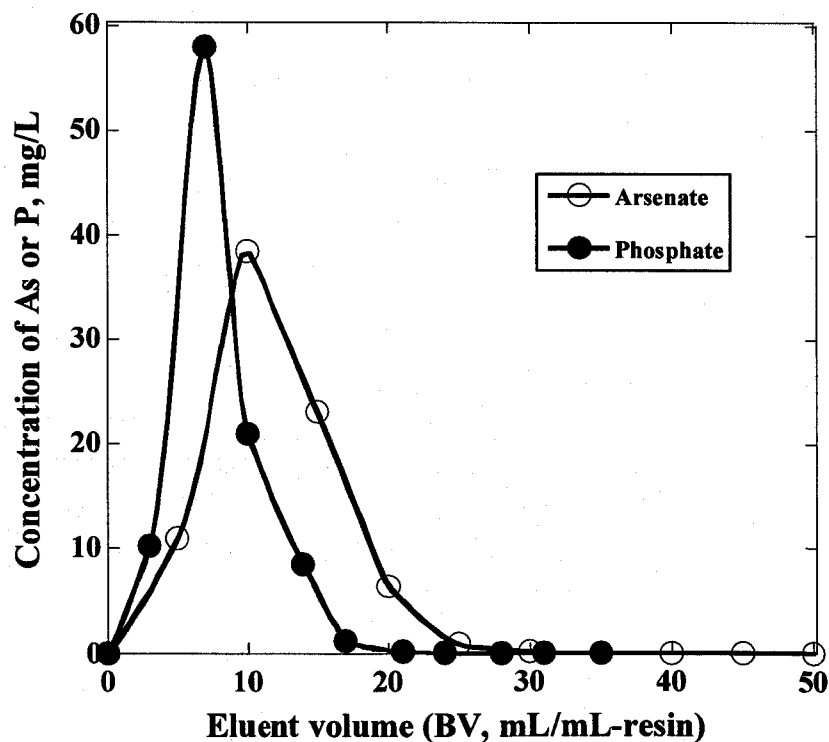
Figure 3-4- Elution of adsorbed arsenate and phosphate from Zr(IV) loaded MPR column with 0.1 M NaOH. Eluent flow rate: 3 h^{-1}. For detailed arsenate and phosphate adsorption operations refer to entry no. 8 in Table 3-1 and entry no. 16 in Table 3-2, respectively.

3.1.4. Conclusions

Column-mode uptake of arsenate and phosphate by Zr(IV) loaded MPR was studied under various conditions. The maximum arsenate adsorption was observed in acidic media at pH 2 and 3. Even in neutral pH region, the Zr(IV) loaded MPR worked well. All results were obtained using the same column for 4 months. No Zr(IV) was found during many cycles of adsorption and elution operations. However, very little amount of Zr(IV) was found in the column effluents when the column was regenerated by 0.5 M sulfuric acid solution. The presence of competing anions (chloride and sulfate) does not interfere with arsenate uptake, an enhancement uptake rate is observed. In the case of phosphate adsorption, The Zr(IV) loaded adsorbent worked well to remove phosphate from water in the presence of chloride, bicarbonate and sulfate at the flow rate of 30 h^{-1}. The adsorbed arsenate and phosphate were quantitatively eluted with 0.1 M sodium hydroxide solution and regenerated by feeding 0.01 M Zr(IV) solution in 0.5 M H_2SO_4. Therefore, the Zr(IV) loaded MPR is an effective to selective removal of trace arsenate and phosphate from water.

Zirconium(IV) loaded bifunctional fiber containing both phosphonate and sulfonate as arsenate and phosphate adsorbent

3.2. Removal of arsenate

3.2.1. Introduction

In many countries, high arsenic (As) concentrations in alluvial aquifers become problem, and in particular, both alluvial and deltaic aquifers in Ganges delta area contain As at the most serious concentration levels (Smedley and Kinniburgh, 2002). Several arsenic adsorbents have been proposed to purify water contaminated with As. Ferric oxides and alumina were not able to use repeatedly and generate secondary problems from sludge containing arsenic. Ligand exchangers based on metal ion loaded chelating resins can adsorb arsenate selectively and the adsorbed arsenate can be eluted with some pertinent eluents. For instance, Zhu and Jyo proposed a ligand exchange adsorbent for arsenate and arsenite on the basis of Zr(IV) loaded cation exchange resins having phosphoric acid and phosphonic acid groups (Zhu and Jyo, 2001a; Jyo et al., 2005a). Several groups have also proposed arsenate adsorbents by loading metal ions such as Fe(III), Zr(IV), Mo(VI) and Cu(II) onto chelating resins such as iminodiacetic acid resins and their homologs (Chanda et al., 1988; Suzuki et al., 2000a; Seko et al., 2004; Balaji et al., 2005; An et al., 2005; Matsunaga et al., 2005; Mondal et al., 2006). However, one of the most serious drawbacks of granular arsenic adsorbents is low kinetic performances in uptake of arsenate. Opposed to granular adsorbents, fibrous adsorbents have excellent kinetic performances in uptake of a target ion. Indeed, Seko et al. (2004) have reported a fibrous arsenate adsorbent, which was obtained by loading Zr(IV) onto a monofucntional cation exchange fiber prepared by graft polymerization of vinyl monomers containing phosphoric acid groups. This fibrous adsorbent exhibits excellent kinetic performances but unfortunately its columnar uptake of arsenate was tested in relatively high concentration levels of 5 – 10 mM of arsenate (370 – 750 mg/L of As). However, concentrations of arsenate are not so high in arsenic contaminated groundwater even in Ganges delta area and are less than 2 mg/L. In this connection, we have already developed a bifunctional cation exchange fiber containing both phosphonic and sulfonic acids (named FPS, **Scheme 3-2**) (Jyo et al. 2005b). This

work was planned in order to clarify the behavior of Zr(IV) loaded FPS in column mode uptake of arsenate in the lower concentration levels of 0.016 − 0.15 mM (1.2 − 11 mg of As/L).
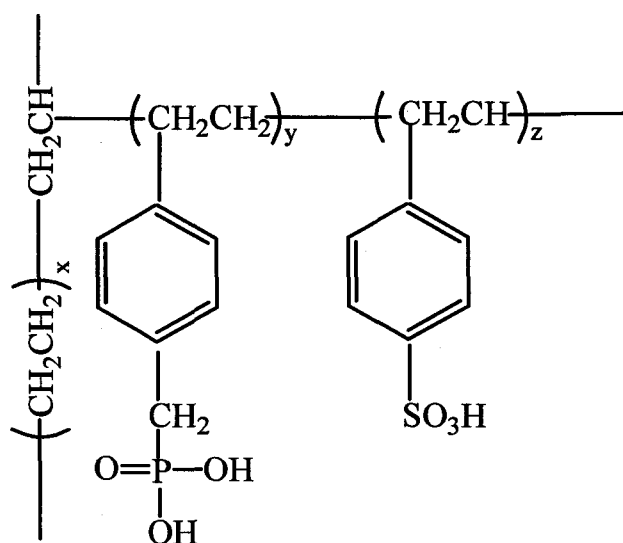
Scheme 3-2- Bifunctional cation exchange fiber (FPS)

3.2.2. Experimental

3.2.2.1. Materials

Polyethylene coated polypropylene staple fiber (0.9 denier, length 3.8 cm) was provided by Kurashiki Textile MFG Co., Osaka, Japan. Chloromethylstyrene (CMS) was provided from Seimi Chemical Co. Chigasaki, Japan. Styrene (ST) was purchased from Wako Pure Chemical Co. Reagents were of guaranteed grade and ultra-pure water was used unless otherwise noted. CMS and ST were co-grafted onto polyethylene coated polypropylene fibers by means of electron irradiation induced liquid phase graft polymerization in which equimolar mixture of CMS and ST was used in their liquid phase graft co-polymerization onto the trunk fiber. The detailed procedures for the graft polymerization and preparation of FPS were described elsewhere (Jyo et al., 2005b).

Weight increase in graft polymerization was 1.3 times that of the trunk fiber. The acid capacity, phosphorus and sulfur contents were determined by reported methods (Maeda and Egawa, 1984; Zhu and Jyo, 2001b). The acid capacity of FPS is 4.9 meq/g and its phosphorus and sulfur contents were 0.99 and 2.1 mmol/g, respectively.

3.2.2.2. Preparation of Zr(IV) loaded bifunctional fiber

Loading of Zr(IV) onto FPS was conducted by column method. A dried sample of FPS (0.4 g) was packed into polyethylene column (i. d. 1.3 cm) and FPS was swollen for 24 h in water. Then the FPS bed in the column was pressed with a glass rod with a flat end until the bed height became constant. The volume of the wet fiber bed in the column was 2.0 mL. The Zr(IV) solution was prepared by dissolving $Zr(SO_4)_2 \cdot 4H_2O$ into an aqueous H_2SO_4 (0.5 M). Then, acidic 0.01 M Zr(IV) solution (0.5 M H_2SO_4) (96 mL) was fed to the column. After washing the column with 0.5 M H_2SO_4 (30 mL) and with water (20 mL) in successive, 0.2 M NaOH solution (40 mL) was fed to the column. After the column was washed with water (20 mL) and then with 0.5 M H_2SO_4 (30 mL), acidic 0.01 M Zr(IV) solution (0.5 M H_2SO_4) (96 mL) was fed to the column for more loading of Zr(IV). This series of operations were repeated three times. Flow rate of all solutions and water was 3 h^{-1} in space velocity (SV), which is designated by the ratio F/V$_{bed}$; here F is flow rates of solutions or water in mL/h and V$_{bed}$ is a volume of the fiber bed. All column effluents were collected on a fraction collector, and concentration of Zr(IV) in each fraction was measured by ICP-AES. Amount of immobilized Zr(IV) was calculated from the concentration difference between feeding solution and column effluents.

3.2.2.3. Column-mode adsorption and elution of arsenate

Arsenate feed solutions were prepared by dissolving $Na_2HAsO_4 \cdot 7H_2O$ in water. The pH of feed solutions was adjusted by spiking a dilute H_2SO_4. Before adsorption operation of arsenate, the Zr(IV) loaded fiber packed column was conditioned to be the same pH as that of arsenate feed solutions. Arsenate feed solutions were fed to the column at a given flow rate. After the column was washed with water, adsorbed arsenate was eluted by feeding 0.1 M NaOH to the column at a flow rate of 5 h^{-1} in SV. After washing

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the column with water, the column was regenerated by feeding 0.5 M H_2SO_4 for the next use. All effluents were collected on a fraction collector and arsenic and zirconium concentrations in each fraction were determined by ICP-AES. Arsine hydride generation method was used when the concentration of As in feed solutions was 1.2 mg/L. The 1% breakthrough point was designated as the feed volume supplied to the column up to $C/C_0 = 0.01$, where C_0 and C represent concentrations of As in feeds and in column effluents, respectively. Volumes of solutions or water supplied to the columns in adsorption-elution-regeneration operations are expressed by unit of bed volumes (BV), which is designated by the ratio, $V_{supplied}/V_{bed}$; here $V_{supplied}$ is volumes of solutions or water in mL.

3.2.3. Results and discussion

3.2.3.1. Zirconium (IV) loading onto FPS

The pKa_1 of phosphonic acid is 2 – 3. Then dissociation of phosphonic acid group on the grafted polymer chains will be depressed below pH 1, resulting in folding of grafted chains on which phosphonate groups are fixed in the case of the monofunctional phosphonate fiber. In case of the bifunctional phosphonate/sulfonate fiber, on the other hand, 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. The uptake of Zr(IV) by FPS in the first run was 0.57 mmol/g, which is a half of its phosphorus content. The loading procedures of Zr(IV) on FPS were repeated three times as shown in **Figure 3-5**. The total amount of Zr(IV) on FPS after 3 runs increased up to 1.19 mmol/g. **Scheme 3-3** shows one of possible structures around the loaded Zr(IV). As ligand exchanger, Zr(IV) should be retained on FPS without any leakage at wide pH range. In this regard, the column packed with the Zr(IV) loaded FPS was treated with 0.5 M H_2SO_4 or 0.2 M NaOH at the flow rate of 3 h^{-1} in SV and no measurable Zr(IV) was found in the effluents.

3.2.3.2. Effect of flow rate on arsenate adsorption

In case of columns packed with Zr(IV) loaded phosphonic acid and phosphoric acid resins, flow rates of feeds for arsenate removal were around 10 h^{-1} in SV. Fibrous adsorbents generally take up ionic species much faster than granular resins. Then, the effect of flow rate of a feed on breakthrough profiles of arsenate was tested by changing the flow rates of the feed from 10 to 100 h^{-1} in SV. Here, the feed was 0.13 mM arsenate solution of pH 3.0. **Figure 3-6** shows breakthrough profiles of arsenate. Detailed conditions and results are summarized in **Table 3-3** (entry nos. 1 - 8). One percent breakthrough points of arsenate decrease with an increase in the flow rate of the feed. The 1% breakthrough capacity for arsenate was 0.035 mmol/g at the flow rate of 10 h^{-1} in SV but it decreased down to 0.027 mmol/g at the flow rate of 100 h^{-1} in SV. However, the 1% breakthrough capacity for arsenate was not significantly affected up to the flow rate of 50 h^{-1}. Indeed, the 1% breakthrough capacities for arsenate at flow rates of 20 and 50 h^{-1} were 0.032 and 0.030 mmol/g, respectively. If the adsorption of arsenate is controlled by diffusion of arsenate in fiber phases, breakthrough profiles of arsenate must be flow-rate independent up to flow rates of 1000 h^{-1} as in the case of uptake of heavy metal ion by several chelating fibers (Seko et al., 2004). However, breakthrough profiles of arsenate are flow rate dependent. This means that the ligand exchange reaction is not so fast or the diffusion of arsenate is not as fast as those for uptake of the metal ions by the chelating fibers. At the present, it is difficult to judge which the real causes of the flow rate dependent breakthrough profiles.
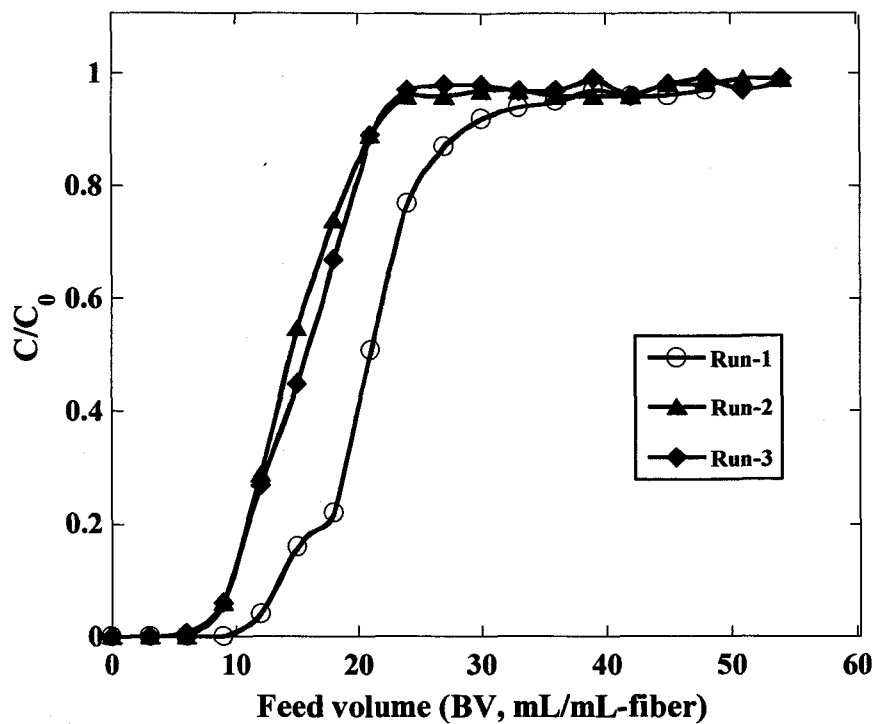
Figure 3-5- Loading of Zr(IV) onto bifunctional fiber (FPS). 0.1 M of Zr(IV) solution in acidic media was supplied to the FPS packed column at a flow rate of 3 h^{-1}.
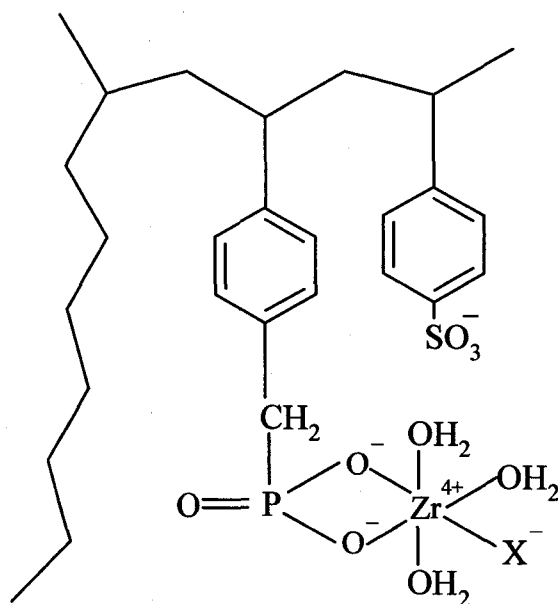
Scheme 3-3- Possible bonding of Zr(IV) with FPS
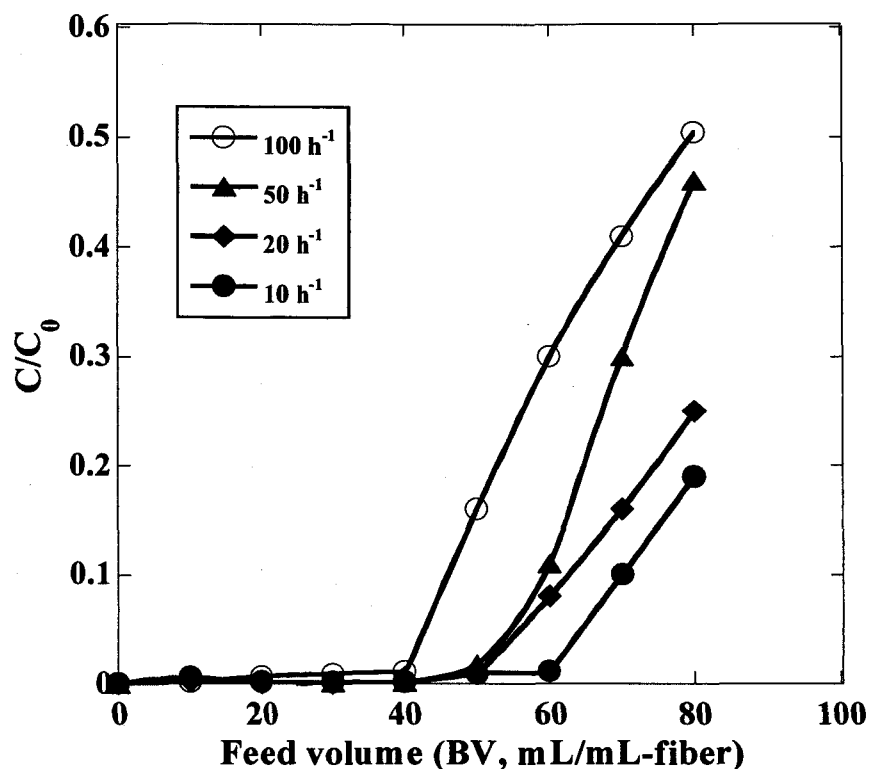
Figure 3-6- Effect of flow rate of feed on breakthrough profiles of arsenate. Feed: 0.13 mM of arsenate, pH 3. For detailed conditions and numerical results refer to entry nos. 1 – 8 in Table 3-3.

3.2.3.3. Elution of adsorbed arsenate

Since hydroxide is the hardest Lewis base among common inorganic anions, it is expected that aqueous NaOH behave the effective eluting reagent for adsorbed arsenate as already reported (Zhu and Jyo, 2001a). **Figure 3-7** illustratively shows an elution profile of arsenate in the elution operation with 0.1 M aqueous NaOH. The adsorbed arsenate was quantitatively eluted within 30 BV of the eluent. During elution, no measurable Zr(IV) was found in the column effluents. After the elution of arsenate, the column was regenerated by feeding 0.5 M H_2SO_4. The regenerated column was further conditioned by contacting the blank solution, which had the same composition as that of the feed except for arsenate, and then next adsorption-elution-regeneration operations were started.

Table 3-3- Detailed conditions and results on column-mode uptake of arsenate by Zr(IV) loaded FPS under different feed flow rates

Entry no.	Feed volume (BV)	Feed flow rate (h^{-1} in SV)	Feed C_0 of arsenate (mM)	Breakthrough point (BV)	Breakthrough capacity (mmol/g)	Total uptake (mmol/g)	Amount eluted (mmol/g)	Recovery (%)
1	80	10	0.14	54	0.033	0.040	0.041	102
2	80	10	0.14	55	0.035	0.041	0.042	102
3	80	20	0.13	50	0.032	0.038	0.039	103
4	80	20	0.13	49	0.032	0.039	0.039	100
5	80	50	0.13	45	0.029	0.039	0.040	102
6	80	50	0.13	47	0.031	0.037	0.036	97.3
7	80	100	0.14	40	0.027	0.034	0.033	97.1
8	80	100	0.14	39	0.026	0.034	0.035	103
9	675	200	0.016	301	0.024	0.038	0.036	94.7
10	675	200	0.016	303	0.024	0.036	0.035	97.2

Volume of wet fiber bed: 2.0 mL, feed solution pH: 3.0±0.2.

3.2.3.4. Effect of inorganic anions on arsenate adsorption

The most frequently encountered anions in groundwater are chloride and sulfate and less frequently one is nitrate. It is important to check the effect of these anions on uptake of arsenate. Then, solutions containing arsenate (0.13 mM) and a sodium salt of each anion (0.30 mM) were prepared and supplied to the column at the flow rate of 50 h^{-1} in SV. The pH of solutions was kept at 3.0. Detailed conditions and numerical results are summarized in **Table 3-4** (entry nos. 4 and 11 − 16). **Figure 3-8** shows breakthrough profiles of arsenate and suggests that the adsorption of arsenate is not interfered with these anions but breakthrough points are slightly increased by sodium chloride and sodium sulfate. Similar trends were reported by several researchers on arsenate adsorption by metal ion loaded chelating resins (Zhu and Jyo, 2001a; Chanda et al., 1988; Balaji et al., 2005). The Zr(IV) binds with arsenate so strongly that increased concentration of sodium ion from added salts will promote the invasion of arsenate through ion pair formation of arsenate with sodium ion according to reactions (1) and (2).

$$Na^+ + H_2AsO_4^- \rightleftharpoons H^+ + NaHAsO_4^- \tag{1}$$

$$R(SO_3^-)(PO_3^{2-})Zr^{4+}X^- + NaHAsO_4^- \rightleftharpoons$$
$$R(SO_3^-)(PO_3^{2-})Zr^{4+}NaHAsO_4^- + X^- \tag{2}$$
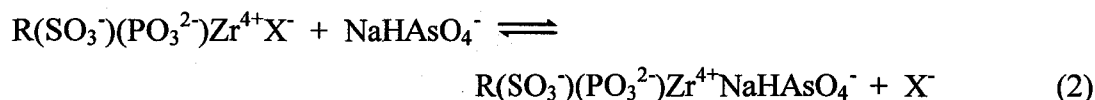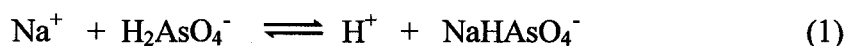
3.2.3.5. Effect of pH on arsenate adsorption

Zr(IV) prefers hydroxide to arsenate. This predicts that uptake of arsenate by the present adsorbent decreases with an increase in pH. Then, the pH effect on arsenate adsorption was tested in the pH range between 2.0 and 5.6. The results are summarized in **Table 3-5** with experimental conditions.

Results in **Table 3-5** suggest that the breakthrough capacity for arsenate was not changed so greatly below pH 3 but gradually decreases with an increase in the pH of the feed between pH 3 and pH 5.6. Arsenate will be adsorbed by Zr(IV) loaded FPS through their coordination to Zr(IV). The anion of weak Lewis base like sulfate is coordinated to Zr(IV) after the regeneration operation with treatment of aqueous H$_2$SO$_4$. The weak Lewis

base sulfate is easily replaced with arsenate species such as $H_2AsO_4^-$ and $HAsO_4^{2-}$. For instance, exchange of sulfate with $H_2AsO_4^-$ can be expressed by the reaction (3).

$$R(SO_3^-)(PO_3^{2-})Zr^{4+}(SO_4^{2-})_{1/2} + H_2AsO_4^- \rightleftharpoons$$

$$R(SO_3^-)(PO_3^{2-})Zr^{4+}(H_2AsO_4^-) + 1/2 (SO_4^{2-}) \qquad (3)$$
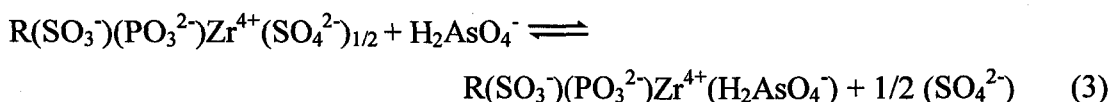
Since hydroxide OH^- is the hardest Lewis base among the anions of interest here, the following ligand exchange reaction (4) shifts to right hand side with an increase in pH:

$$R(SO_3^-)(PO_3^{2-})Zr^{4+}(H_2AsO_4^-) + OH^- \rightleftharpoons$$

$$R(SO_3^-)(PO_3^{2-})Zr^{4+}(OH^-) + H_2AsO_4^- \qquad (4)$$
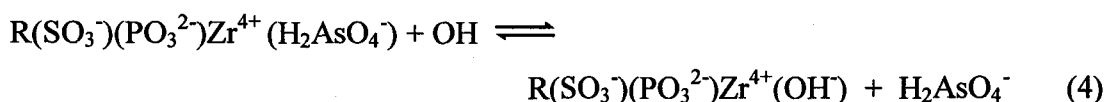
Then, uptake of arsenate decreased with an increase in pH. Above pH 5, however scattering in total uptake of arsenate became marked compared with those below pH 4. This is probably due to that the buffer capacity of the feed is the minimum around ca. pH 4.6. Low buffer capacity will bring unstable pH of the feed leading to rather marked scattering of total uptake of arsenate above pH 4.

3.2.3.6. Rapid adsorption of arsenate from its highly diluted solution

Although arsenic concentrations in groundwater are less than 2 mg/L (Smedley and Kinniburgh, 2002), volumes of arsenic contaminated groundwater are huge. The higher the adsorption rate of arsenate, the shorter the time required for purification of the given volume of contaminated groundwater. Then, the purification of water contaminated with arsenate was tested by feeding a solution containing 0.016 mM arsenate (1.2 mg of As/L, pH 3) to the column at a flow rate of 200 h^{-1} in SV. **Figure 3-9** shows the breakthrough profile of arsenate during adsorption operation. Detailed conditions and numerical results are summarized in **Table 3-3** (entry nos. 9 and 10). The breakthrough point was 302 BV, which correspond to the breakthrough capacity 0.024 mmol of As/g of dried FPS. Even though the concentration of arsenate was as low as 1.2 mg of As/L and the flow rate was as high as 200 h^{-1} in SV, the 1% breakthrough capacity was not decreased in appreciable amounts.

Table 3-4- Conditions and summary of column-mode arsenate uptake by Zr(IV) loaded FPS in the presence of competing anions

Entry no.	Feed			Breakthrough point (BV)	Breakthrough capacity (mmol/g)	Phosphate adsorbed (mmol/g)	Phosphate eluted (mmol/g)	Recovery (%)
	NaCl (mM)	NaNO$_3$ (mM)	Na$_2$SO$_4$ (mM)					
4	-	-	-	47	0.031	0.039	0.040	102
11	0.3	-	-	50	0.032	0.045	0.042	93.3
12	0.3	-	-	51	0.033	0.041	0.042	102
13	-	0.3	-	50	0.033	0.045	0.042	93.3
14	-	0.3	-	50	0.033	0.043	0.042	97.7
15	-	-	0.3	60	0.039	0.050	0.049	98.0
16	-	-	0.3	59	0.038	0.047	0.046	97.8

Wet fibers bed: 2.0 mL, feed solution pH: 3.0±0.2, volume of feed: 80 BV.

Table 3-5- Summary of pH effect on columnar uptake of arsenate by Zr(IV) loaded FPS

Entry no.	Feed		Breakthrough point (BV)	Breakthrough capacity (mmol/g)	Total uptake (mmol/g)	Eluted amount (mmol/g)	Recovery (%)
	solution pH	C_0 of arsenate (mM)					
17	2.0	0.13	40	0.026	0.038	0.036	94.7
18	2.0	0.13	40	0.026	0.043	0.042	97.6
19	3.0	0.13	45	0.029	0.034	0.033	97.1
20	3.0	0.13	47	0.031	0.039	0.040	102
21	4.0	0.15	31	0.022	0.034	0.033	97.1
22	4.0	0.15	31	0.023	0.035	0.034	97.1
23	5.0	0.15	28	0.021	0.026	0.025	96.1
24	5.0	0.15	29	0.021	0.029	0.029	100
25	5.6	0.14	20	0.014	0.027	0.025	92.5
26	5.6	0.14	20	0.014	0.036	0.036	100

Feed (160 BV) was supplied to the column at the flow rate of 50 h^{-1}.
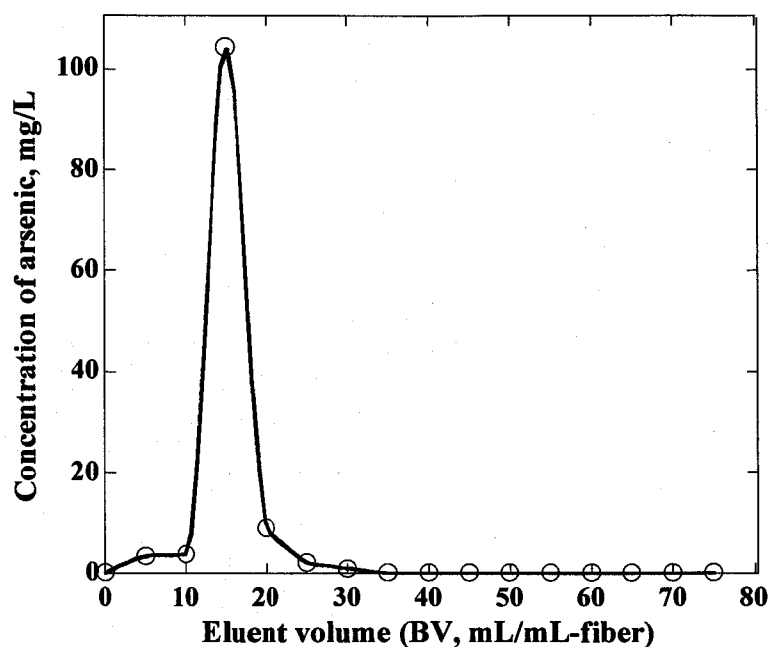
Figure 3-7- Elution of adsorbed arsenate from the Zr(IV) loaded FPS column with 0.1 M NaOH. Flow rate of eluent: 5 h^{-1} in SV. For other conditions refer to entry no. 10 in Table 3-3.
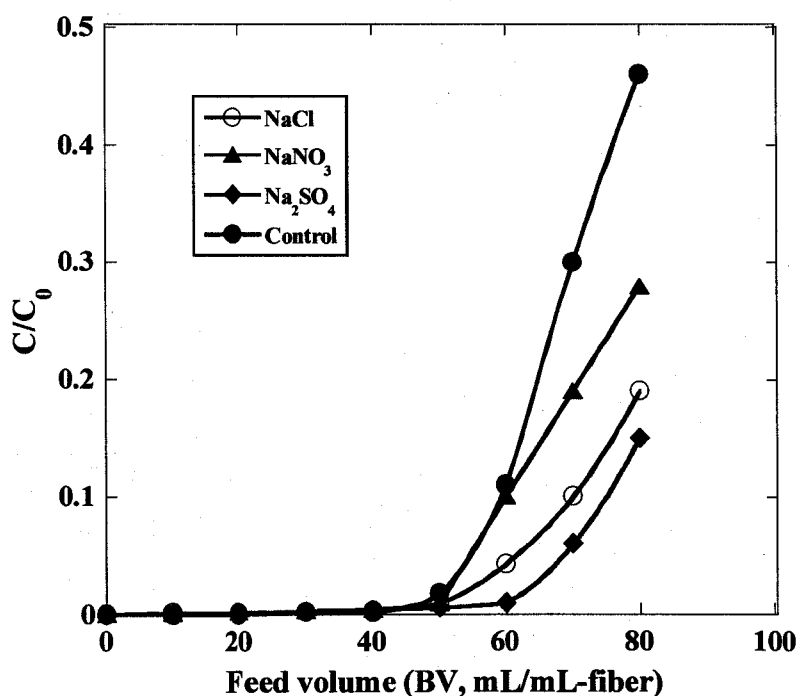
Figure 3-8- Effect of sodium salts on uptake of arsenate. Anions concentration: 0.3 mM, arsenate feed: 0.13 mM and flow rate of feed: 50 h^{-1} in SV. For detailed conditions and results refer to entry nos. in Table 3-4.
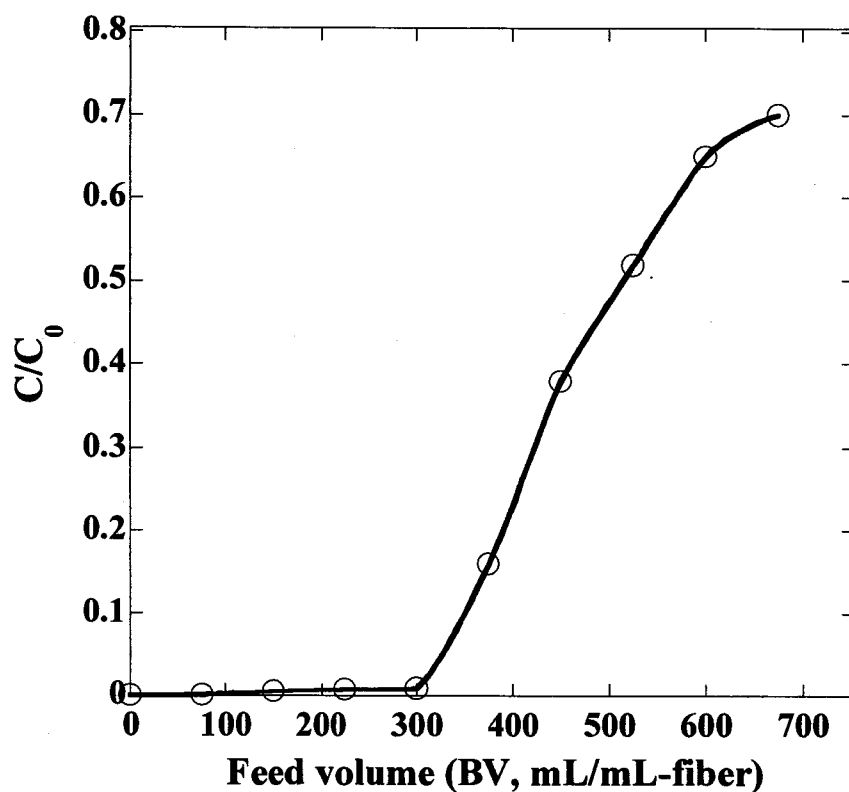
Figure 3-9- Adsorption of arsenate from 0.016 mM arsenate solution of pH 3.0 under a high feeding rate of 200 h^{-1} in SV. For detailed conditions and results refer to entry nos. 9 and 10 in Table 3-3.

All experimental results given in this paper were obtained using the same column for 4 months without change of Zr(IV) loaded FPS and reloading of Zr(IV) as well. During repeated adsorption-elution-regeneration operations, no measurable Zr(IV) was found in the column effluents. This means that the Zr(IV) was strongly retained on FPS. Concentrations of arsenate in groundwater is usually less than 2 mg/L, it is very important to investigate the behavior of the proposed adsorbent in such dilute arsenic concentration levels comparable to those in real groundwater, because breakthrough capacities are affected by kinetic aspects of ligand exchange reactions. The present work clarified that the Zr(IV) loaded FPS fiber is able to purify 300 BV of water contaminated with 1.2 mg/L of arsenic as arsenate for 1.5 h.

3.2.4. Conclusions

This highly selective arsenate adsorbent was prepared by loading Zr(IV) onto a bifunctional fiber containing both phosphonate and sulfonate. This bifuctional cation exchange fiber was prepared by phosphorylation and sulfonation of the precursory trunk fiber, which was co-graft of chloromethylstyrene and styrene onto polyethylene coated polypropylene fiber by electron irradiation induced graft polymerization technique. Arsenate uptake was not affected in the presence of competing anions such as chloride, nitrate and sulfate but slightly enhancement uptake capacity was observed because of ion pair formation of arsenate and added sodium ion. Column-mode work also revealed that uptake of arsenate by Zr(IV) loaded adsorbent was strongly affected by feed flow rates from 10 to 100 h^{-1}. However, the Zr(IV) loaded fiber removed arsenate from a dilute solution containing 0.016 mM arsenate (1.2 mg of As/L) at a flow rate of 200 h^{-1} and breakthrough point was 302 bed volumes, which gives the breakthrough capacity of 0.024 mmol/g. Adsorbed arsenate was quantitatively eluted with 0.1 M sodium hydroxide, and then the column was regenerated by 0.5 M sulfuric acid solution. After conditioning, the column was used for the next arsenate adsorption operation. This Zr(IV) loaded ligand exchange adsorbent can be used to remove arsenate from water for long time without any replacement.

3.3. Removal of phosphate

3.3.1. Introduction

Phosphorus is essential for living organisms. However, huge volume of wastewater production containing high concentration of phosphate is responsible for eutrophication problem of rivers, lakes and inland seas (Morse et al., 1998; Mullan et al., 2006; Onyango et al., 2007; Kabayama et al., 2003). Therefore, discharging high nutrient content wastewater into water bodies, phosphate removal is important to conserve natural aquatic environment. The USEPA has recommended a maximum level of phosphorus in water to be less than 0.05 ppm for controlling eutrophication and Florida Everglades Forever Act recommended a new mandate of 0.01 ppm of phosphorus (P) in water (USEPA, 1986; Florida Everglades Forever Act, 1994).

Several chemical and biological methods have been proposed for the removal of phosphate in water and wastewater. Coagulation and biological methods are used industrial level and these treatment processes are unable to satisfy the mandate level of less than 0.01 ppm (Stante et al., 1997; Vasudevan et al., 2008; Zhao and Sengupta, 1998; Babatunde et al., 2008; Yildiz, 2004; de-Bashan and Bashan, 2004). Therefore, extensive researches have been carried out to develop suitable methods based on stable running, simple operation technique, and high selectivity and kinetic performances. These are adsorption and ion exchange, electrodialysis, and ligand exchange adsorbents such as Zr(IV), Fe(III), Al(III) and Mo(VI) loaded cation exchange and chelating resins (Kuzawa et al., 2006; Ozacar, 2003; Zhu and Jyo, 2005; Chimenos et al., 2003; Seida and Nakano, 2002; Lee et al., 2003; Zhao and Sengupta, 1998, Chitrakar et al., 2006; Wu et al., 2007; Babatunde et al., 2008; Jyo et al., 2008; Genz et al., 2004). Among them, adsorption by selective adsorbents and ligand exchange adsorbents by column-mode process were promising, because they prefer phosphate over naturally occurring anions in water, such as chloride, nitrate, bicarbonate, and sulfate (Zhao and Sengupta, 1998; Hamoudi et al., 2007; Jyo et al., 2008). Fibrous adsorbents have exhibited excellent kinetic performances than granular resin and can be used in high flows rates of feeds containing environmentally unfriendly ions. In addition, they are regenerated completely and usable for many cycles for long term without replacement. The Zr(IV) loaded bifunctional fibrous ligand exchange adsorbent was able to remove arsenate from water at a feed flow rate of 200 h^{-1} from its feed

concentration of 0.016 mM arsenate (1.2 mg of As/L) (Awual et al., 2007). Since chemical properties of phosphoric acid are very close to those of arsenic acid, it is expected that the Zr(IV) loaded fiber will selectively and rapidly take up phosphate. Therefore, this work was planned to evaluate behavior of Zr(IV) loaded fiber in column-mode uptake of phosphate under various conditions. Main objectives of this study are to evaluate (i) selectivity to phosphate over chloride and sulfate in neutral pH region, (ii) loss of Zr(IV) in the effluent both in adsorption and elution operations, (iii) kinetic performance to take up phosphate at high feed flow rate, and (iv) and the regeneration method for long term repeated use.

3.3.2. Experimental

3.3.2.1. Materials

It was already described in details in section 3.2.2.1. However, the acid capacity of bifunctional fiber (FPS) is 4.22 meq/g and its phosphorus and sulfur contents are 0.94 and 1.91 mmol/g, respectively. Ultra-pure water prepared by a Milli-Q Academic-A10 (Nippon Millipore Co., Tokyo, Japan) was used through all experimental works. All reagents were of guaranteed grade unless otherwise specified.

3.3.2.2. Zr(IV) loaded bifunctional fiber

Zr(IV) was immobilized onto FPS by column-mode method. A dried sample of FPS (0.45 g) was packed into polyethylene column (inner diameter 1.3 cm) and FPS was swollen for 24 h in water. After that the FPS was packed in the column and volume of wet fiber bed was 2.12 mL. The Zr(IV) solution was prepared by dissolving $Zr(SO_4)_2 \cdot 4H_2O$ into an aqueous H_2SO_4 (0.5 M). The detail loading procedure was described in section 3.2.2.2. However, the series of loading operations were also repeated three times. Here flow rate of all solutions and water was 4 h^{-1} in space velocity (SV).

3.3.2.3. Column-mode adsorption and elution of phosphate

Phosphate feed solutions were prepared by dissolving $NaH_2PO_4 \cdot 2H_2O$ in water and pH of feed solutions was adjusted by spiking a dilute H_2SO_4 or NaOH when needed. Before starting of phosphate adsorption operation, the column was conditioned to be the same pH as that of phosphate feed solutions. Phosphate feed solutions were supplied to the column at given flow rates. After adsorption operation, the column was washed with water at flow rate of 5 h^{-1} and then elution operation started with 0.1 M NaOH at a flow rate of 4 h^{-1}. After washing the column with water, the Zr(IV) loaded FPS column was regenerated with 0.5 M H_2SO_4 for the next use. All effluents were collected on a fraction collector and phosphorus and zirconium concentrations in each fraction were determined by ICP-AES. The breakthrough point was designated when effluent concentration was at 0.01 mg of P/L. Determination of bed volumes and others information is available in section 3.2.2.3.

3.3.3. Results and discussion

3.3.3.1. Effect of pH on phosphate uptake

The pH of feed solution is one of the important factors affecting the performance of phosphate uptake, because the distribution of phosphate species changes with pH and the different phosphate species have different affinities for the Zr(IV) loaded ligand exchange adsorbent. Then, the behavior of phosphate uptake was investigated in the pH range from 2.01 to 7.01. **Figure 3-10** shows the breakthrough profiles of phosphate as a function of pH of feeds and **Table 3-6** lists detailed experimental conditions and numerical results. Similar to the case of Zr(IV) loaded resin (MPR), the pH increase in feeds brought the decrease in breakthrough points of phosphate and breakthrough capacities for phosphate as well as total uptake of phosphate as judged from entry nos. 1 through 10 in **Table 3-6**. With increase in pH, hydroxide concentration increases so that interference of hydroxide with the hardest Lewis acid anion in water increases resulting in decrease in uptake of phosphate. However, this adsorbent is able to purify ca. 470 BV of water containing 0.4 ppm of P down to less than 0.004 ppm of P even at neutral pH. The results given in **Table 3-6** imply that univalent phosphate or divalent phosphate was taken up by

Zr(IV) loaded FPS fiber by ligand exchange complex reaction as shown in **Scheme 3-4**. Several researchers also reported the same trend for metal ions loaded adsorbents to take up target ions (Zhu and Jyo, 2005; Wu et al., 2007). On the contrary, high breakthrough points and uptake were found in neutral pH area by metal oxide loaded polymeric ligand exchange adsorbent (Zhao and Sengupta, 1998).

3.3.3.2. Effect of flow rate on phosphate uptake

The Zr(IV) loaded FPS has high selectivity to phosphate at neutral pH which is approximate pH of lake and river waters. Then, the neutral pH feed solution was supplied to the column at three different feed flow rates (50 to 150 h^{-1}). These feed flow rates are much higher than the feed flow rates in granular resin packed columns, where the flow rates were used at 10 - 40 h^{-1} to take up target anions. **Figure 3-11** shows the breakthrough profiles of phosphate for the effect of feed flow rate. Breakthrough points of phosphate decreased with an increase in the feed flow rate. The detail experimental conditions and results are summarized in **Table 3-6** (entry nos. 9 through 14). At flow rate of 50 h^{-1}, the breakthrough point was ca. 470 BV and it was ca. 340 BV when the flow rate was 150 h^{-1}. Namely, an increase in the flow rate by 3 times brings the decrease in the breakthrough point by 38%. Similarly, an increase in the flow rate from 50 to 100 h^{-1} reduced the breakthrough points from ca. 470 to ca. 410 BV. This means that an increase in the flow rate by 2 times decrease the breakthrough point by 13%. These results indicate that the ligand exchange reaction is slower than conventional anion exchange and hydrogen bonding interaction (Awual et al., 2008).

3.3.3.3. Effect of competing anions on phosphate uptake

The main anions in lake and river waters are chloride and sulphate, which have possibility to interfere with phosphate uptake by competing for adsorption sites. Then their effect was investigated using phosphate solutions containing competing anions in excess. **Figure 3-12** shows breakthrough profiles of phosphate in evaluation of the effect of competing anions on phosphate uptake. Here, the flow rate of the feed was 50 h^{-1} and phosphate concentration in feeds were from 0.405 to 0.419 mg of P/L. The pH of feeds

was neutral pH. The detail conditions and results are summarized in **Table 3-7** at entry nos. 9 and 15-20. In the presence of 10 mg/L chloride in phosphate feed, phosphate uptake and its breakthrough point were not adversely affected but slightly increased the breakthrough points from 477 to 486 BV. Similarly, in the presence of 10 mg sulfate in phosphate feed, breakthrough point and total uptake were increased and the breakthrough points increased from 477 to 523 BV. However, the enhancement in their breakthrough points between sulfate and chloride were rather marked. In addition, the total uptake of phosphate increased from 0.0469 to 0.0496 mmol/g for chloride and 0.0531 mmol/g for sulfate (**Table 3-7** entry nos. 15 - 20). In the presence of both chloride and sulfate at 10 mg of each, phosphate uptake is nearly equal to one in the presence of 10 mg sulfate only. These results indicate that anion interference effect is so low that co-ion of sodium ions enhances uptake of phosphate according to **Scheme 3-4**; Increase in sodium ion in aqueous phase shifts the equilibrium of **Scheme 3-4** to the right hand side. Several researchers were also reported that phosphate uptake by metal ion or metal oxide loaded ligand exchange chelating resins was not interfered with common anions because of ion pair or outer sphere complex formation (Zhu and Jyo, 2005; Zhao and Sengupta, 1998).

3.3.3.4. Elution of adsorbed phosphate

It was reported that hydroxide is the hardest Lewis base among common inorganic anions and aqueous NaOH behave the effective eluting reagent (Zhu and Jyo, 2005). **Figure 3-13** shows an elution profile of phosphate. Phosphate adsorbed on Zr(IV) loaded FPS was quantitatively eluted with 0.1 M aqueous NaOH. Almost 95 % adsorbed phosphate was eluted within 15 BV of the eluent. In complete elution, ca. 35 BV of eluent was needed. Sodium hydroxide at 0.1 M gave sharp peak in phosphate elution. During elution, no measurable Zr(IV) was found in the column effluents. After the elution of phosphate, the column was regenerated with 0.5 M H_2SO_4 solution at flow rate of 4 h^{-1}. The regenerated column was conditioned for the next adsorption operation and then adsorption-elution-regeneration operations were started.

Table 3-6- Detailed experimental conditions and summary of numerical data of column-mode uptake of phosphate by Zr(IV) loaded FPS

Entry no.	Feed			Breakthrough point (BV)	Breakthrough capacity (mmol/g)	Total uptake (mmol/g)	Eluted amount (mmol/g)	Recovery (%)
	solution pH	flow rate (h^{-1} in SV)	C_0 of phosphate (mg of P/L)					
1	2.01	50	0.411	615	0.0384	0.0558	0.0560	100
2	2.01	50	0.411	634	0.0396	0.0561	0.0582	104
3	3.00	50	0.397	584	0.0353	0.0532	0.0546	103
4	3.00	50	0.397	600	0.0362	0.0533	0.0527	98.8
5	4.02	50	0.385	555	0.0325	0.0503	0.0502	99.8
6	4.02	50	0.385	562	0.0329	0.0499	0.0496	99.4
7	5.12	50	0.396	517	0.0324	0.0477	0.0471	98.7
8	5.12	50	0.396	510	0.0319	0.0481	0.0465	96.7
9	7.01	50	0.405	465	0.0286	0.0468	0.0491	105
10	7.01	50	0.405	477	0.0293	0.0469	0.0475	101
11	6.98	100	0.418	415	0.0264	0.0464	0.0473	102
12	6.98	100	0.418	410	0.0261	0.0458	0.0455	99.4
13	6.95	150	0.411	342	0.0214	0.0404	0.0428	106
14	6.95	150	0.411	336	0.0210	0.0409	0.0417	102

Volume of wet fiber bed: 2.12 mL, feed volume: 943 BV.
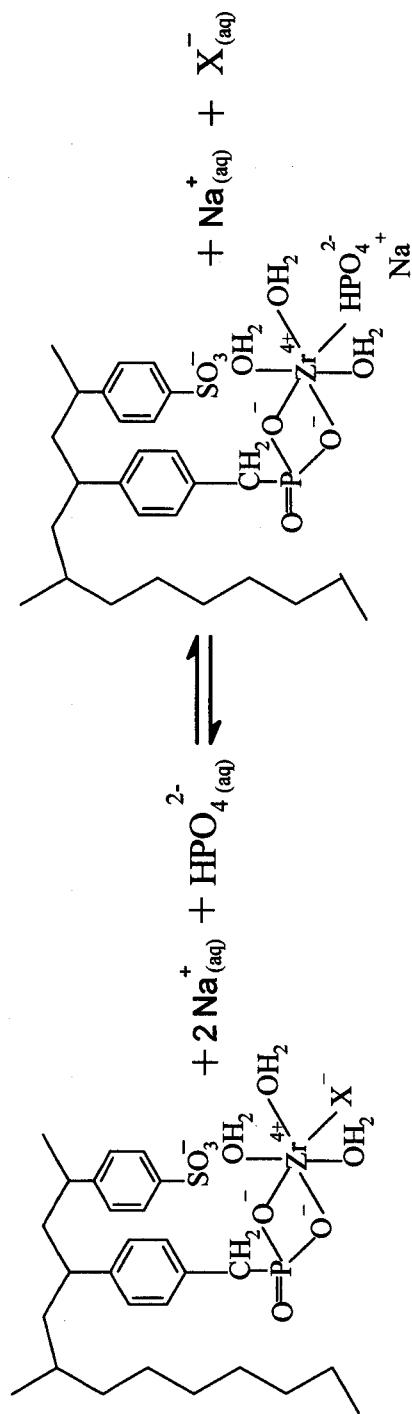
Scheme 3-4- Reaction mechanism of phosphate uptake by Zr(IV) loaded bifunctional fiber (FPS)
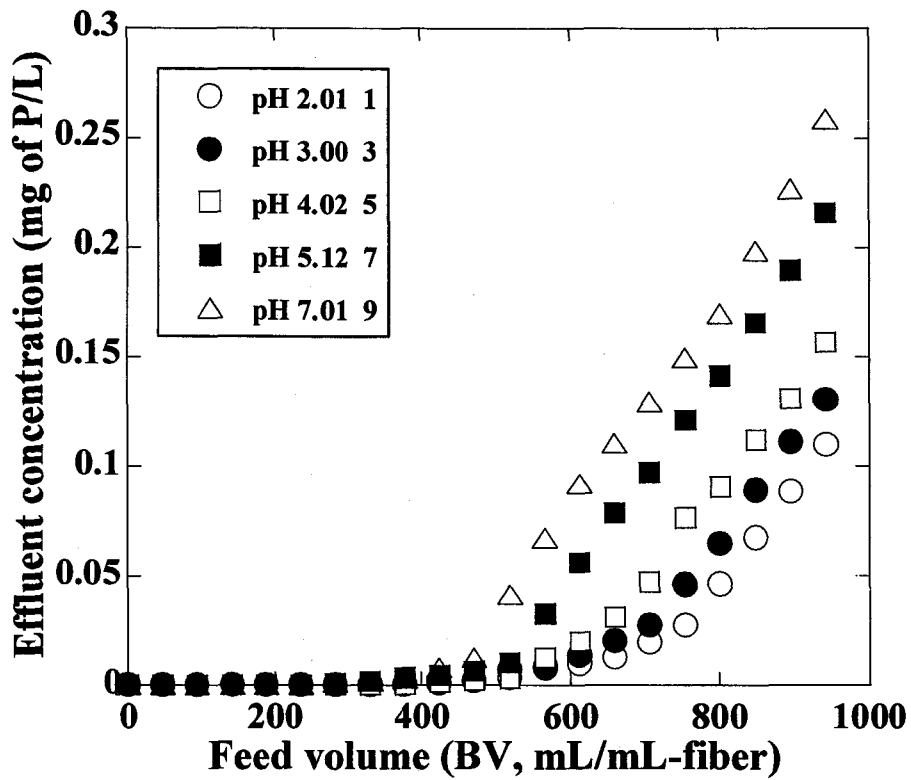
Figure 3-10- Effect of pH of feeds on breakthrough profiles of phosphate. Figure after pH values in inset corresponds to entry nos. 1, 3, 5, 7, and 9 in Table 3-6. For detailed conditions and numerical results refer to entry nos. 1, 3, 5, 7, and 9 in Table 3-6.
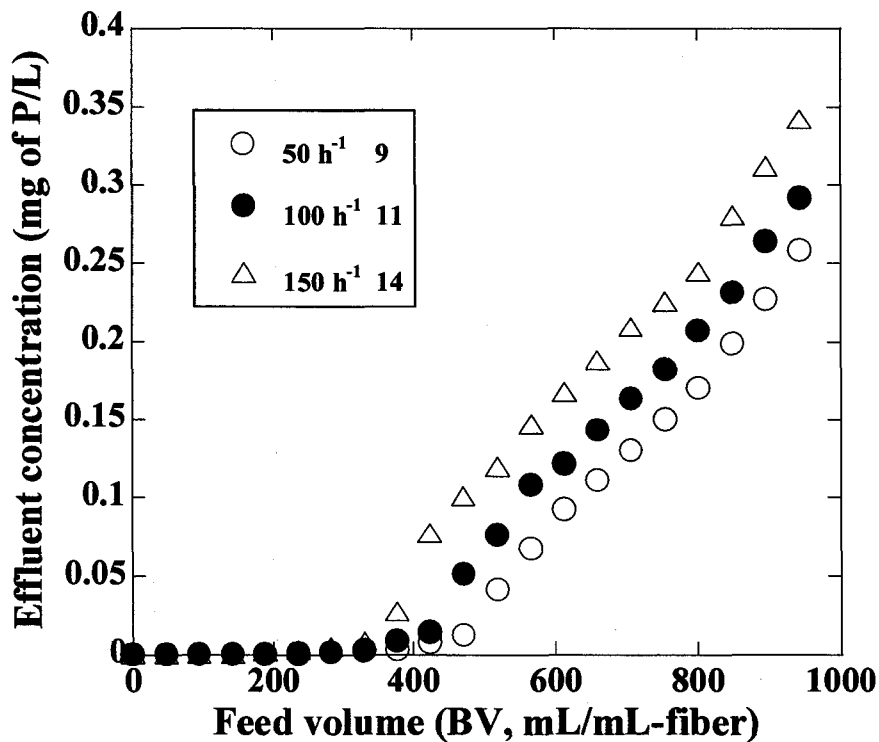
Figure 3-11- Breakthrough profiles of phosphate by Zr(IV) loaded FPS under different flow rates of feed. Figure after flow rate in inset corresponds to entry nos. 9, 11, and 14 in Table 3-6. For detailed conditions and results refer to entry nos. 9, 11, and 14 in Table 3-6.

Table 3-7- Phosphate uptake by Zr(IV) loaded FPS under different concentrations of competing anions and high feed flow rate

Entry no.	Feed					Breakthrough point (BV)	Breakthrough capacity (mmol/g)	Total uptake (mmol/g)	Eluted amount (mmol/g)	Recovery (%)
	C_0 of P (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	flow rate (h^{-1} in SV)					
9	0.405	-	-	-	50	477	0.0293	0.0469	0.0475	101
15	0.412	-	10.0	-	50	483	0.0303	0.0497	0.0507	102
16	0.412	-	10.0	-	50	490	0.0307	0.0494	0.0479	96.9
17	0.419	-		10.0	50	522	0.0333	0.0529	0.0545	103
18	0.419	-		10.0	50	525	0.0335	0.0534	0.0526	98.5
19	0.409	-	10.0	10.0	50	534	0.0332	0.0515	0.0536	104
20	0.409	-	10.0	10.0	50	537	0.0331	0.0519	0.0524	101
21	0.216	15.0	10.0	20.0	250	624	0.0205	0.0268	0.0273	102
22	0.216	15.0	10.0	20.0	250	644	0.0212	0.0271	0.0265	97.8

Wet fibers bed: 2.12 mL, feed solution pH: 6.96 – 7.02, volume of feed: 943 BV.
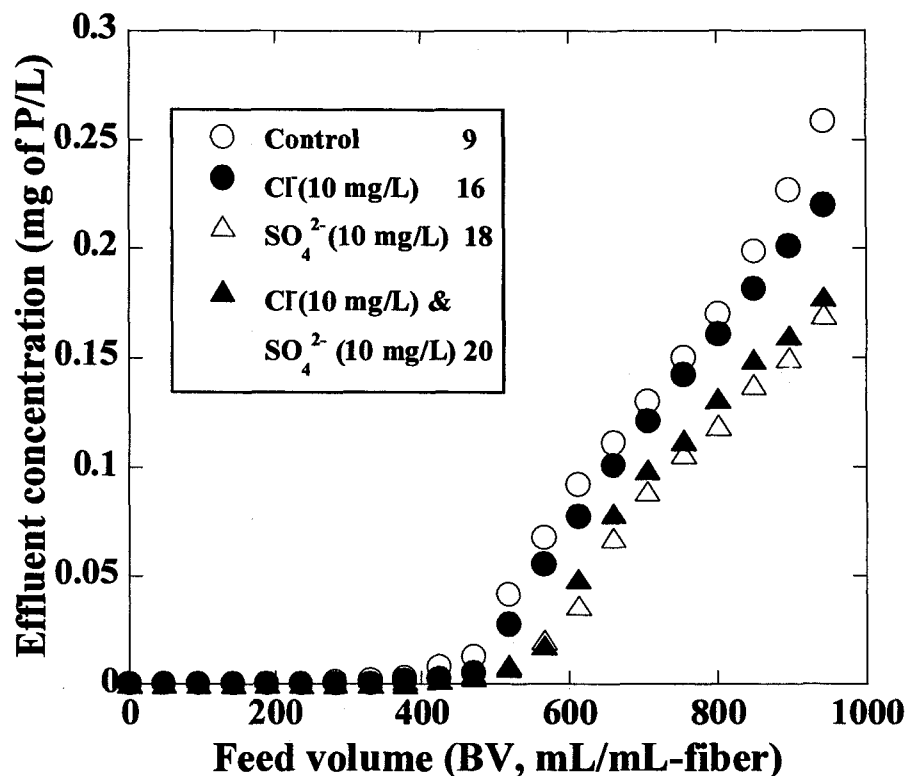
Figure 3-12- Effect of competing anions on phosphate uptake by Zr(IV) loaded FPS column. Figure after explanation of anions in inset corresponds to entry nos. 9, 16, 18 and 20 in Table 3-7. For detailed conditions and results refer to entry nos. 9, 16, 18 and 20 in Table 3-7.
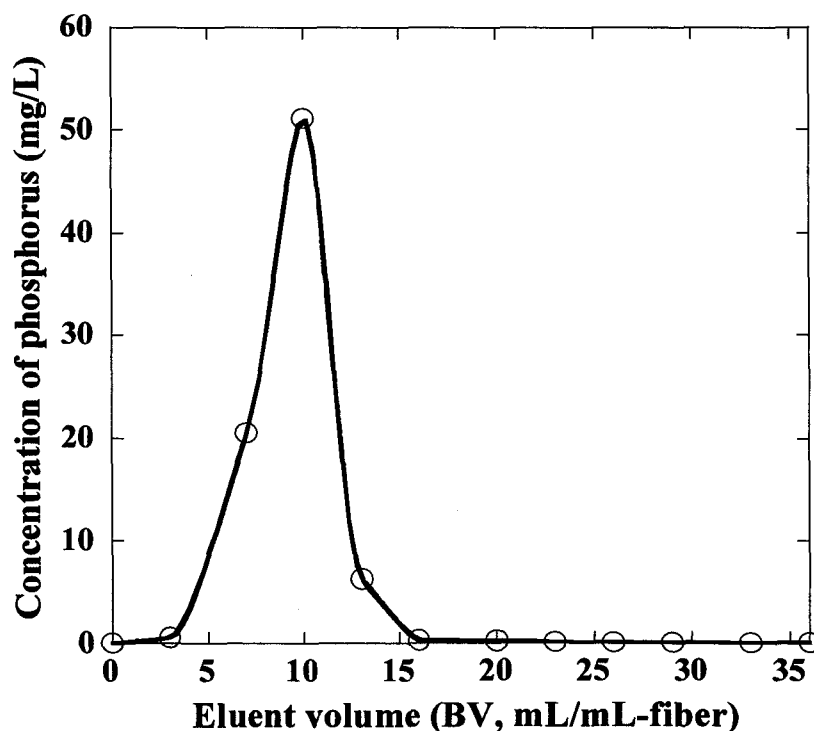
Figure 3-13- Elution of phosphate adsorbed on Zr(IV) loaded FPS column with 0.1 M NaOH at a flow rate of 4 h^{-1}. For detailed conditions and numerical data refer to entry no. 10 in Table 3-6.

3.3.3.5. Rapid removal of phosphate

To remove huge volume trace amount of phosphate from water by column-mode, kinetically excellent adsorbent is preferred. The higher the adsorption rate of phosphate, the shorter the time required for purification of contaminated water. However, phosphate species are co-existed with some anions in wastewater. Therefore, feed solution was prepared with three different competing anions and supplied to the column at feed flow rate of 250 h^{-1}. **Figure 3-14** shows the breakthrough profile of phosphate when phosphate feed was 0.216 mg of P/L and pH 7.02. The detail conditions and results are summarized in **Table 3-7** (entry nos. 21 and 22). The breakthrough point was 634 BV, which corresponds to the breakthrough capacity of 0.0208 mmol/g of dried FPS. However, the concentration of phosphate was as low as 0.216 mg of P/L and the flow rate was as high as 250 h^{-1}, the breakthrough capacity was not decreased sharply compared with flow rate of 150 h^{-1}. However, the feed flow rate of 250 h^{-1} in this work is much higher than the granular resin packed columns.
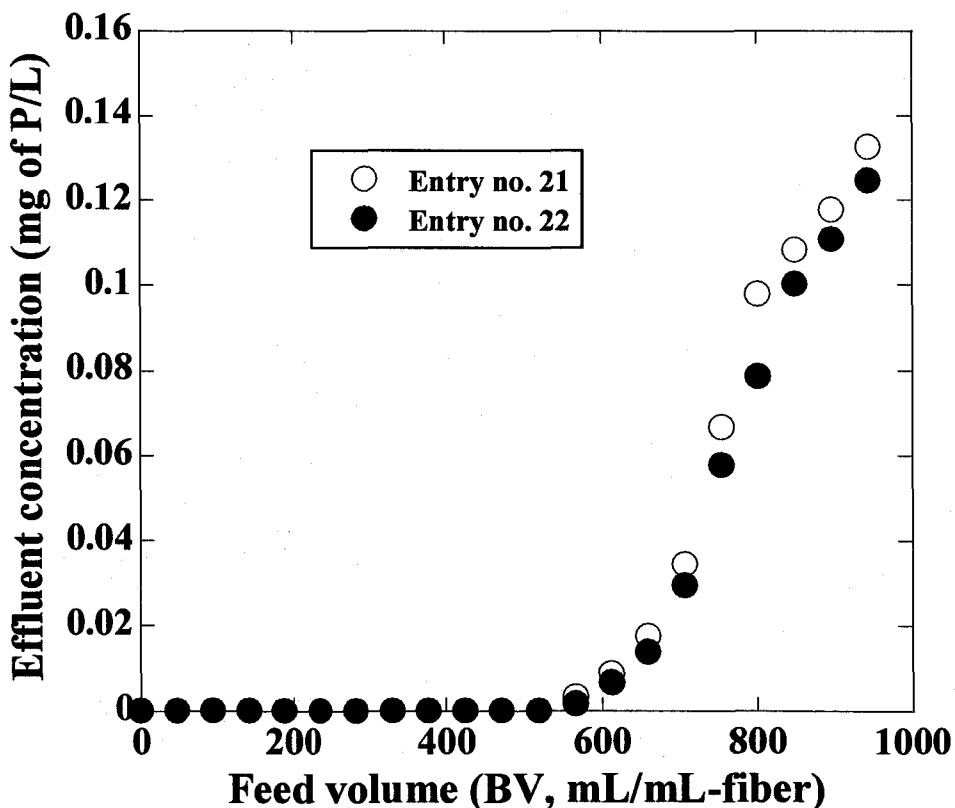
Figure 3-14- Uptake of phosphate from 0.216 mg of P/L solution in the presence of chloride (10 mg/L), bicarbonate (15 mg/L) and sulfate (20 mg/L) at pH 7.02 under a high feed flow rate of 250 h^{-1}. Figure on each profile corresponds to entry nos. 21 and 22 in Table 3-7. For detail conditions and results refers Table 3-7 entry nos. 21 and 22.

All experimental results in the column-mode study were obtained using the same column for 5 months without replacement of Zr(IV) loaded FPS and reloading of Zr(IV) as well. No measurable Zr(IV) was found in the column effluents during many cycles of adsorption-elution-regeneration operations.

3.3.4. Conclusions

Phosphate adsorbent was prepared by loading Zr(IV) onto a bifunctional cation exchange fibers containing phosphonate and sulfonate. Phosphate uptake was tested under various conditions by using a column packed with Zr(IV) loaded FPS. The maximum uptake of phosphate was observed in acidic media at pH 2. Phosphate uptake decreased with an increase in pH of the feeds. Phosphate uptake was not adversely affected with sodium chloride and sodium sulfate but slightly increased uptake was observed, indicating no interference by chloride and sulfate but enhancement effect of co-ion (sodium ion). Phosphate uptake was affected by the flow rate of feed from 50 to 150 h^{-1}; phosphate uptake gradually decreased with an increase in feed flow rate. Zr(IV) loaded FPS was able to take up phosphate from a dilute solution of phosphate as low as 0.216 mg of P/L even at high feed flow rate of 250 h^{-1}. Adsorbed phosphate on Zr(IV) loaded FPS was quantitatively eluted with 0.1 M sodium hydroxide solution, and then the column was regenerated by 0.5 M sulfuric acid solution for next phosphate adsorption operation. All results were obtained using the same column for 5 months and no measurable Zr(IV) was detected in column effluent during repeated cycles of adsorption and elution operations. Zr(IV) loaded ligand exchange adsorbent is effective to remove phosphate from water for long time.

Chapter-4

Removal of arsenate and phosphate from water by poly(allylamine) resin PAA in hydrochloride form

4.1. Arsenate removal

4.1.1. Introduction

Arsenic contamination of groundwater in Ganges delta brings the largest mass poisoning calamity in human history. More than 70 million people in Bengal Basin countries and millions of people in the world are seriously affected by drinking arsenic contaminated water (Chowdhury et al., 1999; Nordstrom D. K., 2002; Smedley and Kinniburgh, 2002; Brown and Ross, 2002; Chakraborti et al., 2003; Mohan and Pittman, 2007). Ingestion of arsenic contaminated water for a long time causes several cancers, such as skin, bladder, and lung cancers, even if the concentration of arsenic is as low as sub-ppm level (Chakraborti et al., 2003; Kartinen and Martin, 1995). Then, USEPA and WHO stringently regulated the allowable maximum arsenic contamination in drinking water to be 10 µg/L (USEPA, 2001; WHO, 1993). Therefore, many methods have been proposed for purification of arsenic contaminated water, such as precipitation of iron coagulation, membrane filtration, and adsorption by arsenic selective adsorbents (Aveston et al., 1958; Meng et al., 2001; Genc-Fuhrman et al., 2005; Kartinen and Martin, 1995; Zaw and Emett, 2002). So far various types of adsorbents have been reported for the removal of arsenic in aqueous solutions; they are activated alumina (Singh and Pant, 2004), activated carbon (Eguez and Cho, 1987; Vaughan and Reed, 2005; Yang et al. 2007), ion exchangers (Horng and Clifford, 1997; Kim and Benjamin 2004; Awual et al., 2008), ligand exchangers obtained by loading Zr(IV), Fe(III), Mo(VI), La(III), and Al(III) onto cation exchange and chelating resins (Chanda et al., 1988; Wasay et al., 1996a; Balaji et al., 2005; Matsunaga et al., 1996; Ohki et al., 1996; Dambies et al., 2000; Zhu and Jyo, 2001a; Awual et al., 2007) and metal oxides based adsorbents (Tokunaga et al., 1997; Raven et al., 1997; Suzuki et al., 2000a; DeMarco et al., 2003; Cumbal and SenGupta, 2005). These studies revealed that ligand exchange adsorbents are promising for arsenic removal due to their high selectivity to arsenate as well as reversibility of adsorption-elution reactions for

their repeated use. However, their main disadvantage is slow kinetics in uptake of anions compared with organic anion exchangers.

Commercially available anion exchange resins having crosslinked poly(styrene) matrices do not prefer highly hydrated anions to lowly hydrated ones, because of hydrophobicity of their copolymer matrices (Lindenbaum et al., 1958; Boyd et al., 1961). Then, these anion exchange resins cannot take up arsenate and phosphate species in the presence of lowly hydrated anions, such as chloride, bromide, nitrate, and iodide (Gregor et al., 1955; Chu et al., 1962; Eliezer and Marcus, 1963). Although organic anion exchangers without aromatic substituents in both polymer backbones and crosslinking moieties are rare (Helfferich, 1962), it is expected that such organic exchangers have different anion selectivity from that of crosslinked poly(styrene) based anion exchangers. Then, we have synthesized fibrous anion exchangers having poly(vinylamine) chains grafted onto trunk polyolefin fibers; these fibrous anion exchangers without any aromatic polymer backbones preferred phosphate and arsenate to chloride and sulfate, in addition to excellent kinetic performances in uptake of anions (Awual et al., 2008). In this regard, crosslinked poly(allylamine) granular resins (PAA) was developed by Nitto Boseki Co. Ltd. PAA was prepared by crosslinking parts of poly(allylamine) with aldehydes. Because of high hydrophilicity of PAA, it resembles fibrous poly(vinylamine) anion exchanger but not conventional anion exchange resins in the anion selectivity as recently reported about its selective and rapid uptake of phosphate (Jyo et al., 2008). These studies led us to study behavior of PAA in column-mode uptake of arsenate. In this work, therefore, column-mode uptake of arsenate by PAA was studied in detail changing pH of feeds from 2.18 to 7.02, concentration of arsenate in feeds from 0.020 to 2.03 mM, and feed flow rates from 250 to 4000 h^{-1} in space velocity. In addition, the effect of chloride, nitrate, and sulfate on uptake of arsenate was examined by changing interferent to arsenate molar ratios in feeds. Finally, competitive uptake of arsenate and phosphate was tested to clarify which anion is more preferred.

4.1.2. Experimental

4.1.2.1. Materials

All chemicals used were guaranteed grade unless otherwise specified. The crosslinked ploy(allylamine) resin, PAA, in hydrochloride form was supplied by Nitto Boseki Co. Ltd., Tokyo, Japan. PAA was developed as reagent for research works. Its chemical structure and fundamental properties are shown in **Table 4-1**. Unfortunately, degree of crosslinking and crosslinker were not disclosed in detail. Arsenic standard solutions (1000 mg/L, As_2O_3 and NaOH in water and then pH 5 with HCl) for ICP-AES calibration curve were purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan. Ultra-pure water prepared by a Milli-Q, Academic-A10 (Nippon Millipore Co., Tokyo, Japan) was used throughout.

4.1.2.2. Measurement of properties of PAA

Chloride content of PAA received as hydrochloride form was determined as follows. First, chloride in PAA in hydrochloride form (1.06 g) was eluted in column-mode with 1 M aqueous sodium hydroxide (80 mL). The effluent was collected into a 200 mL volumetric flask. After acidification of the collected solution with acetic acid (2 M, 80 mL), water was added to the mark. Then, chloride concentration in the acidified solutions was determined by argentometry. In order to change PAA into the free amine form, hydrochloride form PAA was treated with 1 M NaOH in column-mode until the effluent became chloride free, and washed with water until the washing was alkaline free. After air-drying, PAA in the free amine form was dried in vacuum. Nitrogen content of PAA in free amine form was determined by CHN analysis (Engineering Research Equipment Center, Kumamoto University). Dry volumes, wet volumes and water contents of PAA in both hydrochloride and free amine forms were determined by reported methods as described (Helfferich, 1962).

4.1.2.3. Preparation of PAA packed column

PAA in free amine form (0.33 g) was placed into a polyethylene column (inner diameter 1.3 cm). Then, 2 M HCl (80 mL) was fed to the column at a flow rate of 10 mL/h to convert PAA into hydrochloride form. Volume of the resin bed in the column was 1.7 mL when it was equilibrated with 2 M HCl. After drying the resin packed column in a

vacuum, its weight (W_t) was measured. Subtraction of weight of the empty column from W_t indicated that the weight of the hydrochloride form resin was 0.46 g. Then, column was treated with water (120 mL) at a flow rate 24 mL/h, and the arsenate adsorption operation was started. The resin volume in the column just before starting adsorption operation was 2.4 mL; which was greater than that of equilibrated with 2 M HCl because of drastic decrease in ionic strength. Since the resin bed volume changed with solution conditions, the resin bed volume just before the adsorption operation (2.4 mL) was used as the reference volume to convert the flow rate in mL/h into the space velocity (SV) in h^{-1}, and volumes of feeds in mL into bed volumes (BV) in mL/mL-resin. All experiments were repeated twice to check the reproducibility.

4.1.2.4. Adsorption-elution-regeneration operations

Arsenate feeds were prepared by dissolving disodium hydrogenarsenate ($Na_2HAsO_4 \cdot 12H_2O$) in water. The pH of feeds was adjusted with dilute HCl or NaOH when needed. Before adsorption operation in evaluation of the effect of solution acidity, the column was adjusted to be the same pH as that of arsenate feeds. In the case of neutral pH feeds, water (120 mL) was supplied to the column at a flow rate of 10 h^{-1}. After each arsenate adsorption operation, the column was rinsed with water (60 mL) at a flow rate of 20 h^{-1}. The adsorbed arsenate was eluted with 2 M HCl (80 mL) at a flow rate of 4 h^{-1} and the column was simultaneously regenerated into the hydrochloride form during the elution operation. Then, the column was ready for next operation after rinsing with water. All column effluents were collected on a fraction collector and arsenic concentration in each fraction was determined by ICP-AES or ICP-AES connected with Arsine Hydride Generator. The detailed procedures for arsenic determination by ICP-AES and ICP-AES with Arsine Hydride Generation methods were reported elsewhere (Awual et al., 2008). In this work, the breakthrough point is designated as the feed volume in BV supplied to a column up to $C/C_0 = 0.01$. Here, C_0 and C represent concentrations of arsenate in feeds and in the column effluents, respectively. The breakthrough capacity is designated as arsenate uptake in mmol/g-dry resin up to the breakthrough point. Total uptake means uptake of arsenate in mmol/g-dry resin in each adsorption operation.

Table 4-1- Properties of PAA

Functional group	Primary amine ($-NH_2$)
Chemical structure [a]	$-\!\!\left(CH_2\!-\!\!\underset{\underset{NH_2}{\overset{|}{\underset{|}{CH_2}}}}{\overset{|}{CH}}\right)_n\!\!-$
Particle size (diameter) [b]	0.13 - 0.18 mm
Swelling ratio [b]	3.46 (HCl form) and 2.89 (free amine form)
Resin type	Gel
Color	Pale yellow
Water content [b]	69%
Chloride content [b] (as received)	10.2 mmol/g
Nitrogen content [b] (free amine form)	14.6 mmol/g

[a] Crosslinker and degree of crosslinking were not disclosed in detail. [b] Determined in this work.

4.1.3. Results and discussion

4.1.3.1. Properties of PAA

Table 4-1 lists properties of PAA. Its functional group contents in free amine form and chloride contents in hydrochloride form are 14.6 mmol/g and 10.2 mmol/g, respectively. The functional group content is much higher than those of commercially available crosslinked poly(styrene) based ion exchange resins (Helfferich, 1962). In addition, PAA has high swelling properties in both free amine and hydrochloride forms. The provided resin in hydrochloride form has diameters of 0.13 – 0.18 mm in dry state and it highly swells in water. For instance, apparent volume of PAA dry resin in hydrochloride form was 1.30 mL/g and its volume swollen with water increased to 4.50 mL/g. On the other hand, dry resin volume in free amine form was 1.06 mL/g and its volume increased up to 3.06 mL/g in water. Therefore, particle sizes in wet state are larger than those of the dry state. Moreover, water content of PAA in hydrochloride form was 69%. These parameters prove that PAA has high hydrophilicity because of chemical structures consisting of alkane backbone chains bearing hydrophilic aminomethyl groups at high density; leading to non-Hofmiester behavior in uptake of anions. Since sizes of water swollen particles were so large that the high feed flow rates were achieved using a peristaltic pump without high pressure loss as will be described in later sections.

4.1.3.2. Effect of pH of feeds

To clarify effect of the pH of feeds on uptake of arsenate, 1.01 - 1.02 mM arsenate feeds with different pH values from 2.18 to 7.01 (850 BV) were fed to the column at a flow rate of 1000 h^{-1}. Figure 4-1 shows the breakthrough profiles of arsenate. PAA worked well within the tested pH range. Detailed conditions and numerical results are summarized in Table 4-2 (entry nos. 1 - 8). Arsenic acid is triprotic and its three dissociation constants are $pKa_1 = 2.19$, $pKa_2 = 6.94$ and $pKa_3 = 11.50$ (Ringbom, 1963). Breakthrough capacity for arsenate and total uptake of arsenate gradually decreased with increasing pH of feeds as judged from Figure 4-1 and Table 4-2 (entry nos. 1 - 8). This is ascribable to combined effects of the increase in fraction of divalent arsenate species and decrease in amount of protonated species of amino groups in PAA with an increase in the

pH of feeds (Helfferich, 1962), which was schematically shown in **Figure 4-2**. Because the dominant arsenate species are monovalent and divalent anions between pH 4.6 and 7.0, the following ion exchange reactions occur (Awual et al., 2008):

$$\overline{R\text{-}NH_3^+ \cdot Cl^-} + H_2AsO_4^- \rightleftharpoons \overline{R\text{-}NH_3^+ \cdot H_2AsO_4^-} + Cl^- \tag{1}$$

$$\overline{2R\text{-}NH_3^+ \cdot Cl^-} + HAsO_4^{2-} \rightleftharpoons \overline{(R\text{-}NH_3^+)_2 \cdot HAsO_4^{2-}} + 2Cl^- \tag{2}$$
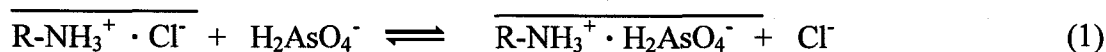
Main arsenate species between pH 2.18 and 4.6 are undissociated H_3AsO_4 and monovalent anion. Then, the following reaction also partly occurs because the column was conditioned with dilute HCl.

$$\overline{R\text{-}NH_2} + H_3AsO_4 \rightleftharpoons \overline{R\text{-}NH_3^+ \cdot H_2AsO_4^-} \tag{3}$$

4.1.3.3. Effect of arsenate concentration in feeds

Effect of arsenate concentration in feeds on breakthrough capacity was tested using feeds containing different concentration of arsenate from 0.492 to 2.03 mM at a feed flow rate of 1000 h^{-1}. Here, amount of supplied arsenate was fixed at ca. 2.0 mmol. **Figure 4-3** shows breakthrough points and capacities for arsenate as a function of the arsenate concentration in the feeds. Detailed experimental conditions and numerical results are given in **Table 4-2** (entry nos. 7 - 12). As judged from **Figure 4-3** and **Table 4-2** (entry nos. 7 - 12), breakthrough points are inversely proportional to the arsenate concentration in feeds. Consequently, breakthrough capacities are not markedly dependent on the arsenate concentration of the feeds. Total uptake of arsenate is also nearly independent of the arsenate concentration in feeds. These results allow estimating a breakthrough point for a feed containing a given concentration of arsenate.

4.1.3.4. Effect of flow rate

Flow rates of feeds in arsenate removal by metal loaded ligand exchange and metal oxides based adsorbents were usually from 10 to 40 h^{-1} (Suzuki et al., 2000; DeMarco et al., 2003; Genc-Fuhrman et al., 2005; Cumbal and SenGupta, 2005). Since the functional group content of PAA is extremely high (14.6 mmol/g), it is expected that high feed flow rates more than 40 h^{-1} will be usable for adsorption operation of arsenate. Then, the flow rate effect on breakthrough capacity for arsenate was investigated changing the feed flow rate from 250 to 2000 h^{-1}. **Figure 4-4** shows breakthrough profiles of arsenate uptake at four different feed flow rates. Detailed experimental conditions and numerical results are given in **Table 4-2** (entry nos. 7, 8 and 13 - 18). The breakthrough capacity decreased markedly with an increase in the feed flow rate (**Figure 4-4** and **Table 4-2** entry nos. 7, 8 and 13 - 18). Although the increase in the flow rate from 250 to 2000 h^{-1} brought 40% decrease in breakthrough capacity, PAA has the breakthrough capacity as high as 2.1 mmol/g even at the high flow rate of 2000 h^{-1}. On the contrary, total uptake of arsenate up to 850 BV of the 1.0 mM arsenate feed did not markedly decrease with an increase in the feed flow rate; the increase in flow rate from 250 to 2000 h^{-1} brought only 6% decrease in total uptake. This is due to the supply of the feed to the column was stopped up to C/C_0 value of 0.1, which means that more than 90% of arsenate fed to the column was taken up by PAA column even at the highest flow rate of 2000 h^{-1}. At this flow rate, breakthrough capacity to functional group content ratio is 0.144; this indicates that only 14.4 % of the functional groups located at near surfaces of resin particles can take up arsenate but the remaining majority of the functional groups do not work up to the breakthrough point. However, the breakthrough capacity as high as 2.1 mmol/g at the feed flow rate of 2000 h^{-1} is very attractive from practical standpoint, because most granular resins and ligand exchange adsorbents do not have high breakthrough capacities under feed flow rates more than 40 h^{-1}. High breakthrough capacities of PAA for arsenate at high flow rates come from combination of extremely high functional group contents and high swelling of PAA in hydrochloride form; the former gives high capacities and the latter does rapid diffusion of anionic species in the resin particles.

Table 4-2- Column-mode uptake of arsenate by PAA using feeds with different pH values and arsenate concentrations under various flow rates of feeds

Entry no.	Feed				Breakthrough point (BV)	Breakthrough capacity (mmol/g)	Arsenate adsorbed (mmol/g)	Total eluted (mmol/g)	Recovery (%)
	solution pH	flow rate (h^{-1} in SV)	C_0 of arsenate (mM)	volume (BV)					
1	2.18	1000	1.02	850	639	3.45	4.55	4.57	100
2	2.18	1000	1.02	850	634	3.42	4.54	4.64	102
3	4.01	1000	1.01	850	597	3.14	4.43	4.31	97.3
4	4.01	1000	1.01	850	595	3.13	4.42	4.35	98.4
5	5.62	1000	1.01	850	562	2.95	4.39	4.39	100
6	5.62	1000	1.01	850	570	2.99	4.39	4.33	98.6
7	7.01	1000	1.01	850	500	2.61	4.37	4.57	104
8	7.01	1000	1.01	850	493	2.58	4.37	4.38	100
9	6.98	1000	2.03	425	263	2.78	4.42	4.44	100
10	6.98	1000	2.03	425	267	2.82	4.43	4.14	93.4
11	7.02	1000	0.501	1700	974	2.54	4.21	4.27	101
12	7.02	1000	0.492	1700	994	2.54	4.29	4.40	102
13	6.97	250	1.03	850	660	3.53	4.52	4.46	98.7
14	6.97	250	1.03	850	658	3.52	4.51	4.35	96.4
15	6.98	500	1.02	850	598	3.15	4.43	4.48	101
16	6.98	500	1.02	850	583	3.08	4.43	4.42	99.8
17	6.97	2000	0.99	850	412	2.13	4.27	4.22	98.8
18	6.97	2000	0.99	850	405	2.09	4.25	4.03	94.8
19	7.01	4000	0.020	15600	7920	0.832	1.51	1.63	108
20	6.95	4000	0.020	15600	7540	0.783	1.45	1.50	103

Resin wet volume: 2.4 mL.
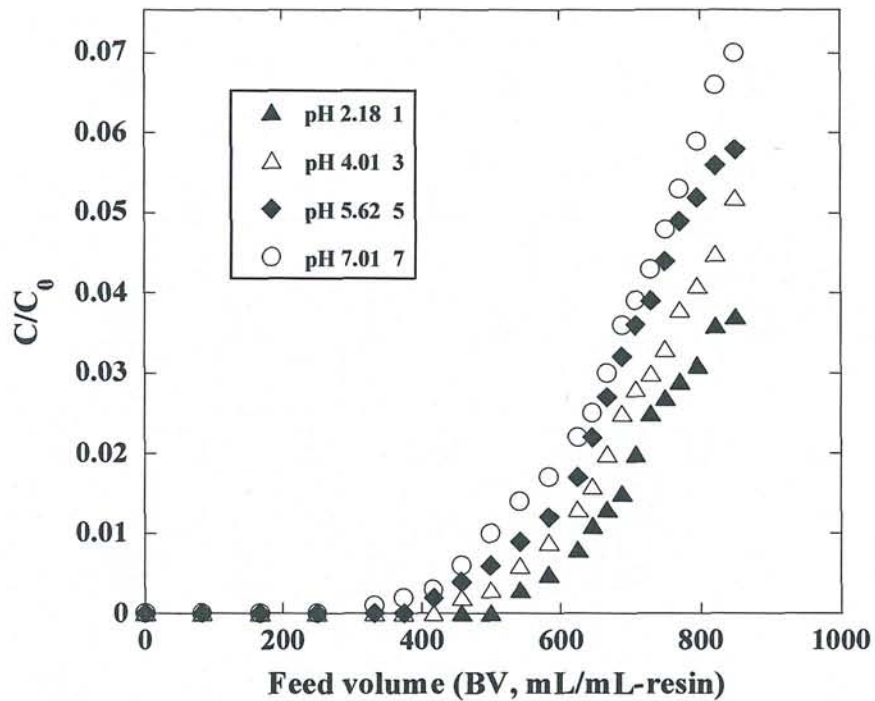
Figure 4-1- Breakthrough profiles of arsenate in its column-mode uptake by PAA using four feeds with different pH values. Figure after pH value in inset corresponds to run no. in Table 4-2. For detailed conditions and results refer to entry nos. 1 - 8 in Table 4-2.
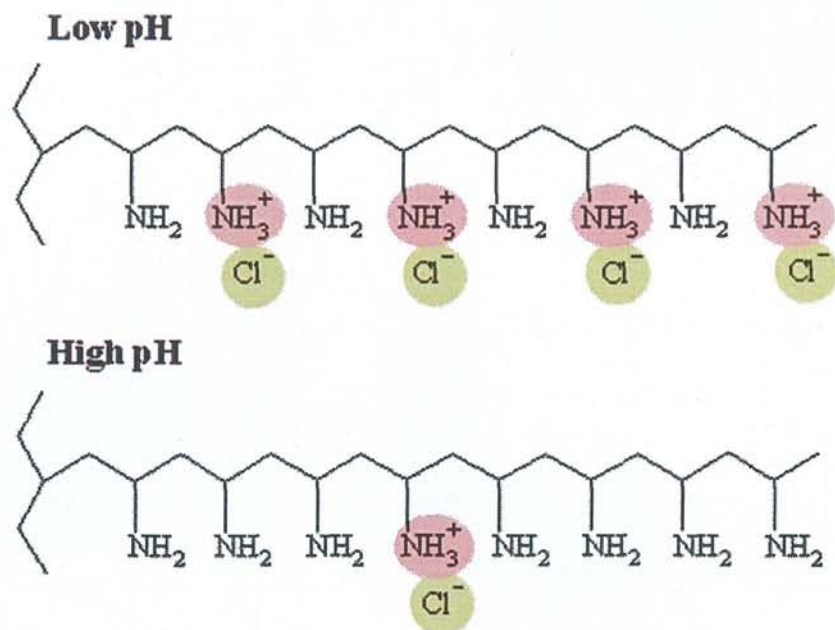
Figure 4-2- Schematic illustration of polyprotonated polyallylammonium sites depends on pH values. At low pH, number of polyprotonated polyallylammonium sites increases and uptake of arsenate was increased.
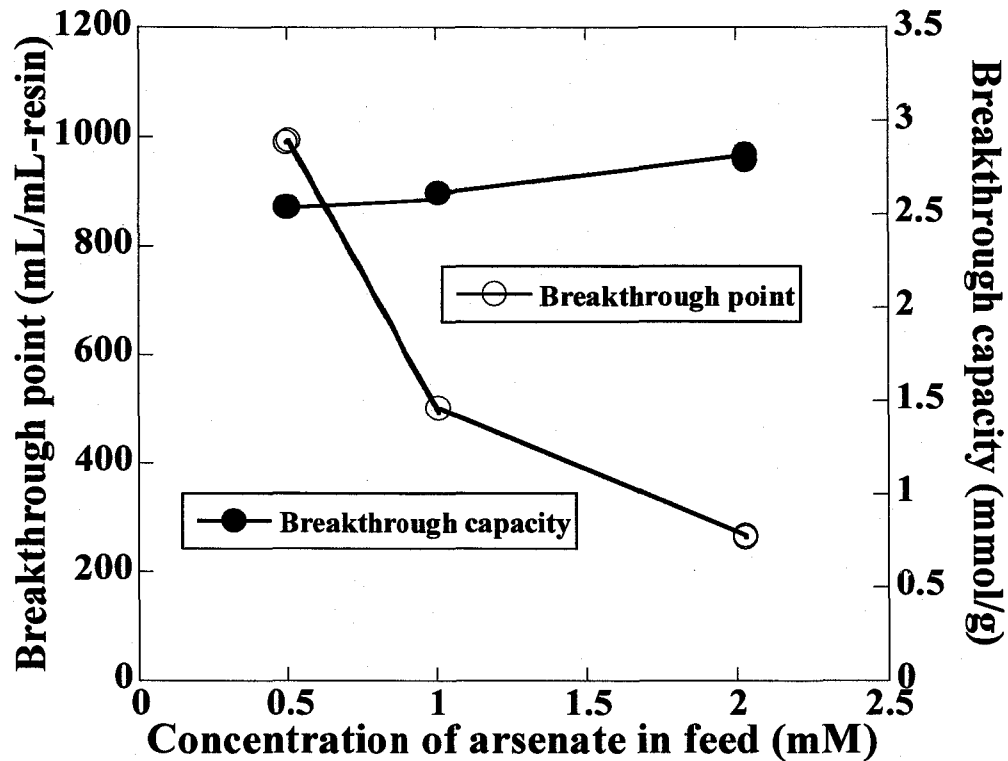
Figure 4-3- Breakthrough points of arsenate and breakthrough capacities of PAA for arsenate uptake as a function of arsenate concentration of feeds. For detailed conditions and results refer to entry nos. 7 - 12 in Table 4-2.
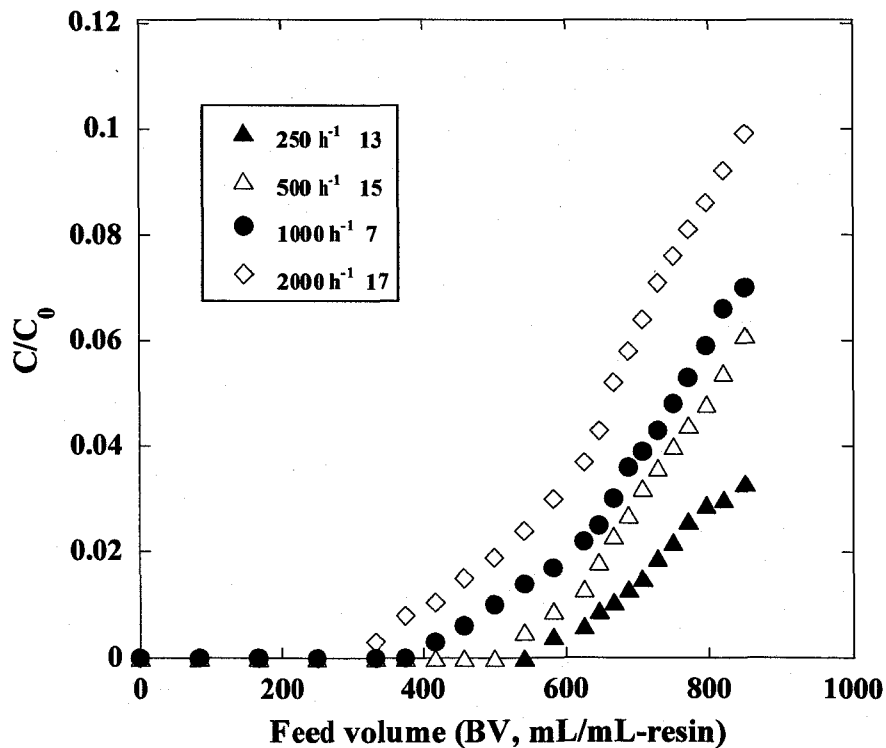
Figure 4-4- Breakthrough profiles of arsenate in its column-mode uptake by PAA as a function of feed flow rate. Figure after flow rate in inset corresponds to entry nos. 7, 13, 15 and 17 in Table 4-2. For detailed conditions and results refer to entry nos. 7, 13, 15 and 17 in Table 4-2.

4.1.3.5. Effect of competing anions

Main anions to be associated with arsenic in groundwater are chloride, sulfate and in some cases nitrate. Then, their effect on uptake of arsenate was tested using feeds containing chloride, nitrate or sulfate as interferent anion. **Figures 4-5(a)** and **4-5(b)** show breakthrough profiles of arsenate in its uptake by PAA from 1.0 mM arsenate feeds containing chloride, nitrate or sulfate at 1 or 5 of the interferent to arsenate molar ratio. **Table 4-3** lists detailed experimental conditions and numerical results. Interference of equimolar chloride or nitrate is not marked, but sulfate more markedly interferes with uptake of arsenate as shown in **Figure 4-5(a)** and **Table 4-3** (entry nos. 21 - 26). **Figure 4-5(b)** shows breakthrough profiles of arsenate in its uptake in the presence of fivefold molar chloride, nitrate, or sulfate; breakthrough points of arsenate decreased markedly compared with those in the presence of equimolar cases. Breakthrough points and capacities in the presence of fivefold chloride or nitrate are interestingly nearly equal to those in the presence of equimolar sulfate. This means that interference by sulfate is nearly fivefold higher than those of chloride and nitrate. In the presence of fivefold sulfate, the breakthrough capacity decreased down to ca. 0.8 mmol/g, which is greater than one fifth of the breakthrough capacity without interferent (ca. 0.6 mmol/g). Then, PAA prefers arsenate to sulfate. Results shown in **Figures 4-5(a)**, **4-5(b)** and **Table 4-3** lead to the selectivity sequence of arsenate > sulfate > nitrate > chloride in column-mode uptake from feeds of neutral pH. On the contrary, strong-base resins are strongly affected by chloride and sulfate (DeMarco et al., 2003). Although ligand exchange adsorbents have much higher selectivity to arsenate over chloride and sulfate (Ohki et al., 1996; Zhu and Jyo, 2001a; DeMarco et al., 2003; Suzuki et al., 2000; Cumbal and SenGupta, 2005), their kinetic performance is far from that of PAA.

4.1.3.6. Uptake of trace arsenate at high feed flow rate

To purify huge volume water contaminated with trace arsenate by column-mode method, the adsorbent should have kinetically excellent performances. The high feed flow rate shortens the time required for purification operations. Moreover, the arsenic concentration in water in Ganges delta areas is usually 0.5 through 3.0 mg/L (Smedley and Kinniburgh, 2002; Chakraborti et al., 2003). Then, 0.020 mM arsenate solution (1.52 mg

of As/L) was supplied to the column at a flow rate of 4000 h^{-1} (9.6 L/h). **Figure 4-6** shows breakthrough curves of arsenate. Detailed conditions and numerical results are given in **Table 4-2** (entry nos. 19 - 20). The breakthrough point is ca. 7700 BV, which corresponds to the breakthrough capacity of 0.808 mmol/g. This means that the column having 2.4 mL wet resin bet was able to purify 19.0 L of water contaminated with arsenate as 1.52 mg of As/L down to less than 10 µg of As/L for 2.0 h. Thus, PAA can rapidly remove low concentration level arsenate, although ca. 6% of functional groups were active to take up of arsenate at the high feed flow rate of 4000 h^{-1}.

4.1.3.7. Competitive uptake of arsenate and phosphate

PAA also selectively removed phosphate from water at high feed flow rate of 3500 h^{-1} as reported (Jyo et al., 2008). Chemical properties of arsenic and phosphoric acids are close each other; for instance, both acids have nearly equal dissociation constants. Therefore, the competitive uptake of arsenate and phosphate was examined using the feed contained 1.0 mM of each. The pH was adjusted to 6.98. **Figure 4-7** shows breakthrough profiles of arsenate and phosphate. Detail conditions and numerical results are given in **Table 4-4** (entry nos. 33 and 34). As anticipated, breakthrough capacity and total uptake of arsenate are nearly equal to those of phosphate, respectively. However, PAA slightly prefers phosphate to arsenate as judged from data given in **Table 4-4**. Similar tendency was observed in the competitive uptake of arsenate and phosphate by a weak anion exchange fiber having grafted poly(vinylamine) chains. However, it seems that poly(allylamine) based anion exchangers are superior to those based on poly(vinylamine), because poly(allylamine) with methylene spacers between polymeric backbones and amino groups have advantages in both protonation to amino groups and flexibility for hydrogen bonding of phosphate and arsenate species with protonated sites.

4.1.3.8. Elution, regeneration and reuse

The adsorbed arsenate on PAA was quantitatively eluted with 2 M HCl at a flow rate of 4 h^{-1} as judged from recoveries of arsenate listed in Tables 4-2, 4-3, and 4-4, although the optimization for elution operations was not conducted. **Figure 4-8** shows an

Table 4-3- Column-mode uptake of arsenate by PAA in the presence of competing anions under competing anion to arsenate molar ratios of 1 or 5

Entry no.	C_0 of arsenate in feed (mM)	Breakthrough point (BV)	Breakthrough capacity (mmol/g)	Total uptake (mmol/g)	Eluted amount (mmol/g)	NaCl (mM)	NaNO$_3$ (mM)	Na$_2$SO$_4$ (mM)	Recovery (%)
15	1.02	598	3.15	4.43	4.48	-	-	-	101
21	1.00	505	2.62	4.19	4.18	1.00	-	-	99.7
22	1.00	508	2.64	4.22	3.94	1.00	-	-	93.3
23	0.99	448	2.31	4.11	4.18	-	1.00	-	102
24	0.99	452	2.33	4.23	4.14	-	1.00	-	97.8
25	1.02	373	1.97	3.39	3.42	-	-	1.00	101
26	1.02	371	1.96	3.48	3.36	-	-	1.00	96.5
27	1.00	372	1.94	3.63	3.75	5.00	-	-	103
28	1.00	373	1.95	3.68	3.62	5.00	-	-	98.3
29	1.01	337	1.77	3.43	3.32	-	5.00	-	96.8
30	1.01	333	1.75	3.42	3.47	-	5.00	-	101
31	1.01	153	0.799	1.39	1.36	-	-	5.00	97.8
32	1.01	149	0.779	1.39	1.38	-	-	5.00	99.2

Column: volume of wet resin 2.4 mL, volume of feed: 850 BV, flow rate of feed: 500 h^{-1}, pH of feeds: 7.00 ± 0.04.

Table 4-4- Competitive uptake of arsenate and phosphate by PAA using a feed containing arsenate and phosphate at 1.00 mM of each

Entry no.	Breakthrough point (BV)		Breakthrough capacity (mmol/g)		Total uptake (mmol/g)		Eluted amount (mmol/g)		Recovery (%)	
	Arsenate	Phosphate	Arsenate	Phosphate	Arsenate	Phosphate	Arsenate	Phosphate	Arsenate	Phosphate
33	370	448	1.92	2.34	3.43	3.80	3.53	4.01	103	105
34	364	444	1.89	2.32	3.40	3.79	3.47	3.77	102	99.5

Feed volume: 1250 BV, pH: 6.98, flow rate of feed: 150 h^{-1}.
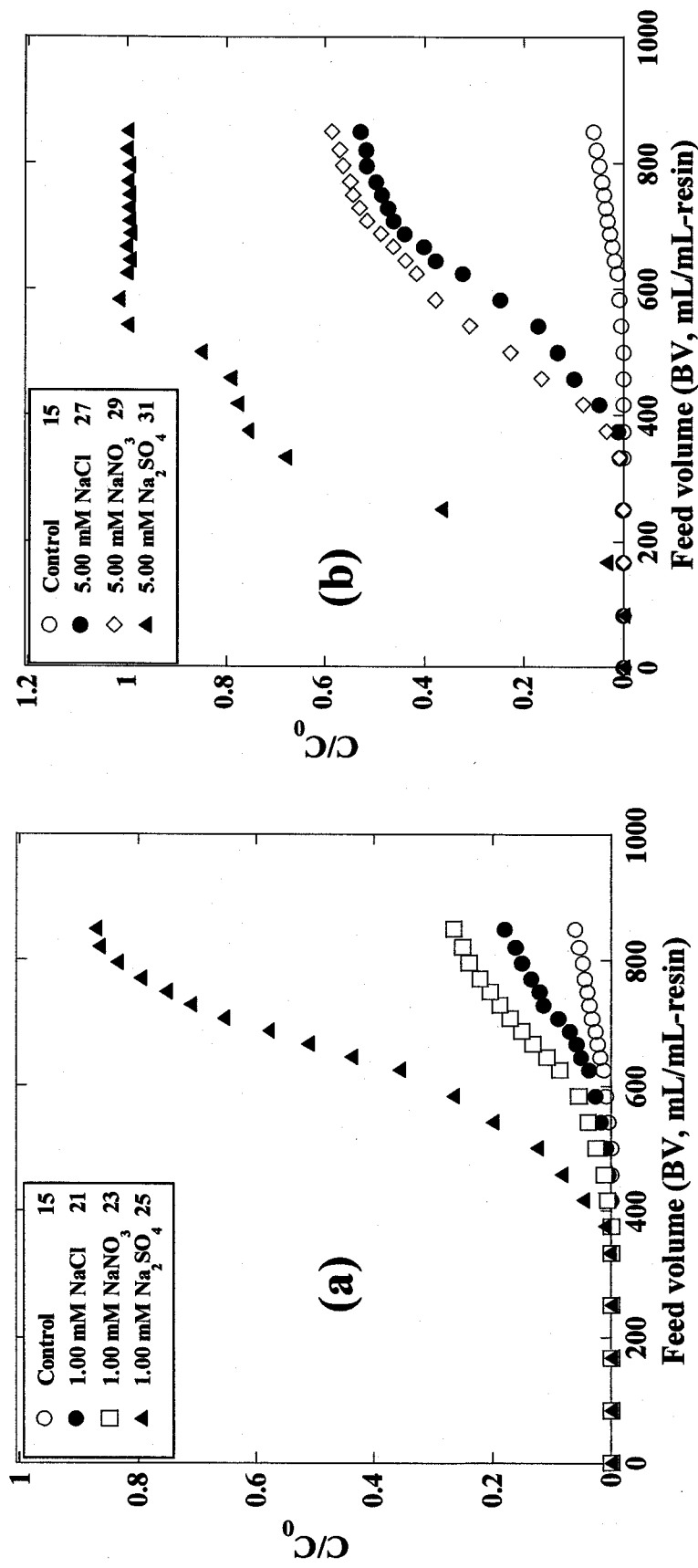
Figure 4-5- Breakthrough profiles of arsenate by PAA in column-mode uptake of arsenate in the presence of chloride, nitrate or sulfate. Feeds 1.00 mM of arsenate. (a) in the presence of 1.00 mM of chloride, nitrate or sulfate; (b) in the presence of 5.00 mM of chloride, nitrate or sulfate. For detailed conditions and results, refer to Table 4-3. Figure after the explanation of each symbol in inset means entry no. in Table 4-3.
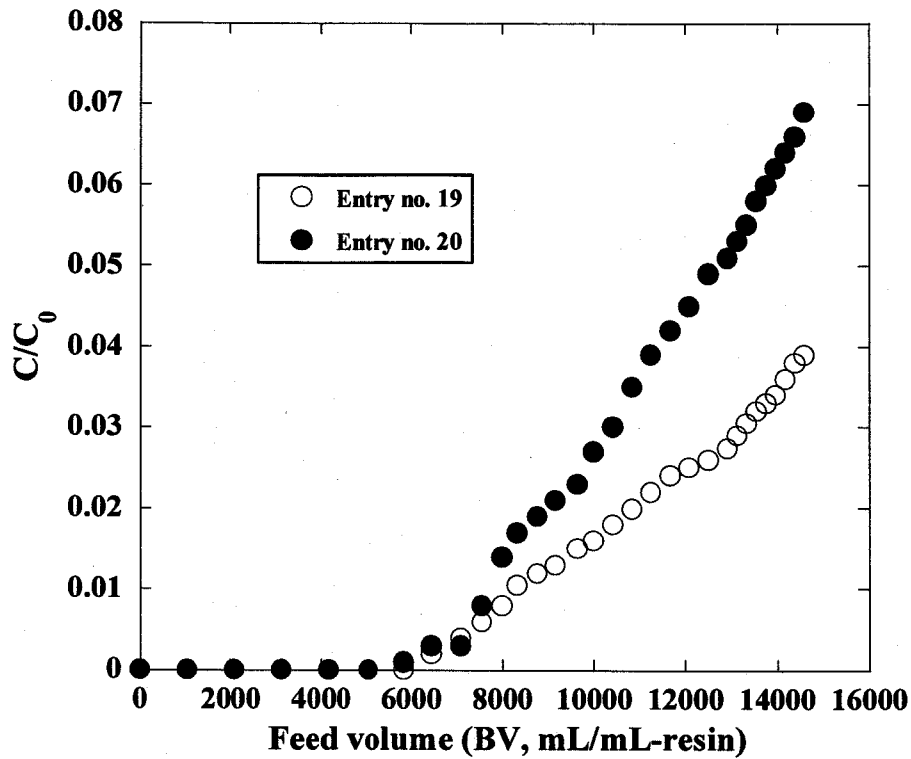
Figure 4-6- Breakthrough profile of arsenate in its column-mode uptake by PAA from a 0.020 mM arsenate feed at feed flow rate of 4000 h^{-1}. Figure in inset corresponds to entry nos. 19 and 20 in Table 4-2. For detailed conditions and results refer to entry nos. 19 and 20 in Table 4-2.
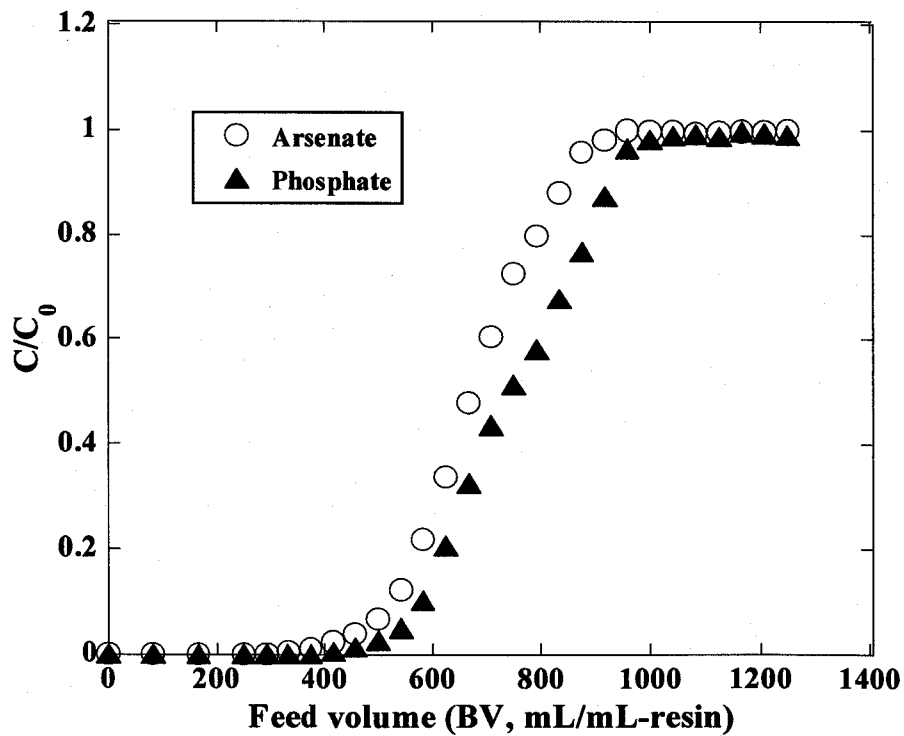
Figure 4-7- Competitive uptake of arsenate and phosphate by PAA. Feed: concentration of arsenate and phosphate at 1.00 mM of each, pH 6.98, flow rate 150 h^{-1}. For detailed conditions and numerical results refer to entry no. 33 in Table 4-4.

example of the elution curve of arsenate. The elution of adsorbed arsenate can be expressed by the following reactions (4) and (5).

$$\overline{R\text{-}NH_3^+ \cdot H_2AsO_4^-} + HCl \rightleftharpoons \overline{R\text{-}NH_3^+ \cdot Cl^-} + H_3AsO_4 \tag{4}$$

$$\overline{(R\text{-}NH_3^+)_2 \cdot HAsO_4^{2-}} + 2HCl \rightleftharpoons \overline{2R\text{-}NH_3^+ \cdot Cl^-} + H_3AsO_4 \tag{5}$$
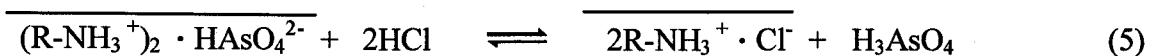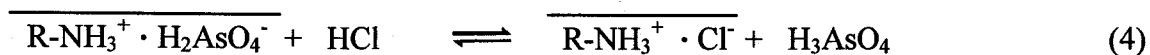
Since pKa_1 of arsenic acid is 2.19, arsenate species are completely converted into the non-charged arsenic acid H_3AsO_4 at pH less than 0 (2 M HCl). The electrically neutral species H_3AsO_4 was easily replaced by chloride ion, resulting in simultaneous regeneration of the resin into hydrochloride form. Consequently, the column can be reused for next adsorption operation after rinsing with water to remove remaining hydrochloric acid in the column.
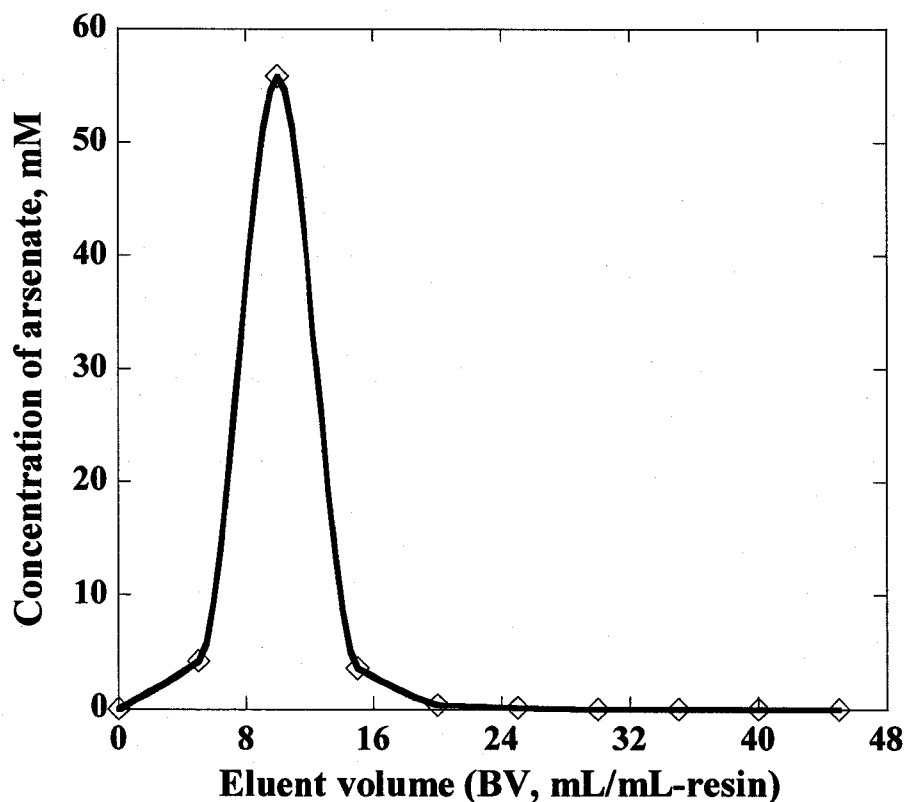
Figure 4-8- Elution curve of arsenate in eluting operation with 2 M HCl at flow rate of 4 h^{-1}. For detailed conditions and numerical results, refer to entry no. 20 in Table 4-2.

All results were obtained using the same column without change of the packed resin and any deterioration in column performances for four months. During many cycles of adsorption-elution-regeneration, no change was observed of PAA resin packed column. It proved that the PAA resin has high stability to withstand of high feed flow rate and can be used for long time to remove arsenate from water without any replacement. Consequently, PAA will be promising for rapid removal of both arsenate and phosphate from water.

4.1.4. Conclusions

Properties of PAA as arsenate adsorbent were studied by column-mode method. First, breakthrough capacities of this resin for arsenate were evaluated by changing conditions of adsorption operations: pH of feeds from 2 to 7, concentration of arsenate in feeds from 0.02 to 2.0 mM, and flow rate of feeds from 250 to 4000 h^{-1}. The breakthrough capacities decreased with an increase in pH of feeds. For instance, when 1.0 mM arsenate feeds of pH 2 and 7 were fed at flow rate of 1000 h^{-1}; respective breakthrough capacities were 3.4 and 2.6 mmol/g. This pH dependency is ascribable to combined effects of the decrease in protonated sites and the increase in divalent anionic species of arsenate with an increase in pH of feeds. When the concentration of feeds was decreased from 2.0 to 0.020 mM, breakthrough capacities decreased from 2.8 to 0.81 mmol/g. Breakthrough capacities were flow rate dependent and decreased from 3.5 to 0.81 mmol/g when flow rate of the feed was increased from 250 to 4000 h^{-1}. Next, the effect of chloride, nitrate, and sulfate on uptake of arsenate from 1 mM arsenate feeds was examined in the presence of equimolar or fivefold molar of each foreign anion. The interference of chloride and nitrate was minor. Although PAA preferred arsenate to sulfate, sulfate markedly interfered with uptake of arsenate. Test of competitive uptake of arsenate and phosphate revealed that PAA slightly preferred phosphate to arsenate. These anion selectivity studies clarified that PAA exhibits non-Hofmeister anion selectivity behaviour different from conventional anion exchange resins based crosslinked poly(styrene) matrices, which cannot take up arsenate and phosphate in the presence of chloride, nitrate, and sulfate in excess. Furthermore, it seems that poly(allylamine) based anion exchangers are superior to those based on poly(vinylamine), because poly(allylamine), which has methylene spacers between polymeric backbones and amino groups, have advantages in both protonation to

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amino groups and flexibility for hydrogen bonding of phosphate and arsenate species with protonated sites. These characteristics bring a high breakthrough (dynamic) capacity as well as excellent kinetic performances. During many cycles of adsorption-elution-regeneration, no deterioration in column performances was observed. It proved that PAA has high stability to withstand high feed flow rate of 4000 h^{-1}. Thus, the PAA is one of promising resins to remove arsenic from water, so long as the effective oxidation method of arsenite will be developed.

4.2. Removal of phosphate

4.2.1. Introduction

Eutrophication is considered as one of the most important environmental problems and phosphate is one of key compounds responsible for eutrophication. Although phosphorus (P) is one of intrinsic elements for the growth of plants and animals, excess amounts of P in water will enhance eutrophication problems (Danalewich et al., 1998; Trepanier et al., 2002). Thus removal of phosphate from water is very important to save not only human beings but also plants and animals. Therefore, the concentration of phosphate in water is limited to below 10 ppb P to escape from eutrophication problems (Florida Everglades Forever Act, 1994; Zhao and Sengupta, 1998; Blaney et al., 2007).

Several methods have been proposed to remove phosphate from water; these include chemical precipitation and adsorption by various adsorbents and microorganisms (Carlsson et al., 1997; Morse et al., 1998; Danalewich et al., 1998; Donnert and Salecker, 1999; Akay et al. 1998; Hongshao and Stanforth, 2001; Kuzawa et al., 2006; de-Bashan and Bashan, 2004; Yang et al., 2006). As chemical precipitation and biological removal processes are not able to remove phosphate to the mandate level or below 10 ppb of P, a variety of adsorbents have been developed. Most of these are ion exchange resins and fibres (Ruixia et al., 2002), ligand exchangers, such as metal ion loaded cation exchange and chelating resins (Wasay et al., 1996b; Zhao and Sengupta, 2000; Henry et al., 2004; Zhu and Jyo, 2005; Shin et al., 2004; Biswas et al., 2007), and metal oxide loaded resins (Zhao and Sengupta, 1998; Tanada et al., 2003; Genz et al., 2004; Zeng et al., 2004; Blaney et al., 2007). The metal ion and metal oxide loaded adsorbents have not been used at high feed flow rates because of their slow kinetic uptake of phosphate. Strong-base anion exchange resins prefer chloride, nitrate, and sulfate to phosphate and show the Hofmeister anion selectivity sequence because of the high hydrophobicity of their crosslinked styrene-divinylbenzene copolymer matrices. On the contrary, we have found that a weak-base anion exchange fibre, FVA, having hydrophilic polyvinylamine chains exhibits a high selectivity to arsenate over chloride and sulfate, when polyvinylamine chains are protonated (Awual et al., 2008). This non-Hofmeister behaviour of protonated

FVA comes from the high hydrophilicity of the FVA matrix as well as hydrogen bonding interaction between $-NH_3^+$ and $HAsO_4^{2-}$ in addition to the conventional anion exchange mechanism (Awual et al., 2008). Since polyallylamine is very close to polyvinylamine, non-Hofmeister anion selectivity can be expected in case of a crosslinked polyallylamine resin in the protonated form.

In this work, we have studied the behaviour of a crosslinked polyallylamine resin (PAA) for the uptake of several inorganic anions in both batch and column modes.

4.2.2. Experimental

4.2.2.1. Materials

The crosslinked polyallylamine resin, PAA, in the hydrochloride form (gel type resin, size: 80 – 115 mesh, dry volume: 1.3 mL/g, wet volume in water: 4.5 mL/g, moisture content: 69 %) was kindly provided by Nitto Boseki Co. Ltd., Tokyo, Japan. Detailed fundamental properties of PAA are shown in **Table 4-1**. Phosphoric acid (85 wt%), $NaH_2PO_4.2H_2O$ and $Na_2HPO_4.12H_2O$ were guaranteed grade and were obtained from Wako Pure Chemical Industries Co., Osaka, Japan. The phosphorus standard solutions were purchased from Wako Pure Chemical Industries Co. Ultra-pure water prepared by a Milli-Q, Academic-A10 (Nippon Millipore Co., Tokyo, Japan) was used in all experimental work. Other chemicals used were guaranteed grade unless otherwise specified.

4.2.2.2. Batch-mode adsorption of phosphate

The resin PAA in the hydrochloride form was treated with 1 M NaOH in column-mode until no chloride was detected in the column effluent and then washed with water until the washings were alkali-free. The resin was first air-dried and then in vacuum. The nitrogen content of PAA in the free amine form determined by CHN analysis was 14.6 mmol/g. The free amine form of PAA thus obtained was used to measure the equilibrium uptake of phosphate as a function of equilibrium pH in the absence and presence of a competing anion. A series of test solutions with various pH values were prepared by

mixing 0.010 M H_3PO_4, 0.010 M NaH_2PO_4, and 0.010 M Na_2HPO_4. The initial analytical concentration of P in the test solutions was 0.010 M. Each test solution (50 mL) was transferred into a series of Erlenmeyer flasks (100 mL) and then PAA (0.050 g) was added to each flask. All the flasks were shaken in a water bath with a mechanical shaker for 24 h at 30 °C and then the pH and P concentration of the supernatant in each flask were measured, using ICP-AES to determine the P concentration. The phosphate uptake by PAA (mmol/g) was calculated from the equation $(C_{initial} - C_{eq})(50/0.050)$ where, $C_{initial}$ and C_{eq} stand for initial and equilibrium concentrations of P in supernatants, respectively.

4.2.2.3. Preparation of PAA packed column

The free amine form of PAA (0.27 g) was placed in a polyethylene column (inner diameter 1.3 cm) and then 2 M HCl (60 mL) was fed into the column at a flow rate of 7 mL/h to convert the resin into the hydrochloride form. The volume of the resin bed was 1.4 mL following equilibration with HCl. Then, the column was washed with water (100 mL) at a flow rate 20 mL/h to remove free hydrochloric acid and the adsorption of phosphate started. The resin volume in the column just before starting adsorption operation was 2.0 mL. Since the resin bed volume changed with solution conditions, the resin bed volume just before the adsorption operation (2.0 mL, bed height 1.5 cm) was used as the reference volume to convert the flow rate from mL h^{-1} into the space velocity (SV) in h^{-1}, and volumes of feeds in mL into bed volumes (BV) into mL per mL resin. Hereafter, flow rates and volumes of solutions and water supplied to the column are denoted by SV and BV, respectively. All column-mode experiments were duplicated to check the reproducibility.

4.2.2.4. Column-mode adsorption elution regeneration cycle

Feed solutions of phosphate were prepared by dissolving $NaH_2PO_4 \cdot 2H_2O$ in water. The pH of feed solutions was adjusted with dilute HCl or NaOH as required. After conditioning of the column (Section 5.2.2.3.), feeds for the adsorption process were supplied to the column at a given flow rate and then the column was washed with water (60 mL) at flow rate of 10 h^{-1}. The adsorbed phosphate was eluted with 2 M HCl at a flow rate of 3.5 h^{-1} and the PAA in the column simultaneously regenerated into the
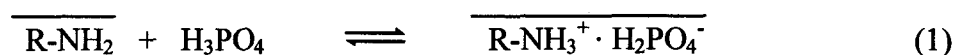
hydrochloride form during elution. Therefore, the column was ready for the next phosphate adsorption operation after washing the column with water as described in Section 5.2.2.3. In the adsorption-washing-elution operations, all the effluents were collected by a fraction collector and the P concentration in each fraction was determined by ICP-AES. The breakthrough point in this work was designated as the feed volume supplied to the column up to $C/C_0 = 0.01$ where, C_0 and C represent concentrations of phosphate in feed and in the column effluent, respectively. The breakthrough capacity was designated as phosphate uptake in mmol/g-resin up to the breakthrough point.

4.2.3. Results and discussion

4.2.3.1. Batch-mode study

4.2.3.1.1. Effect of pH on uptake of phosphate

Uptake of anions by weak-base anion exchange resins and fibres decreases with increase in solution pH, since the number of protonated sites decreases with increase in pH (Awual et al., 2008). **Figure 4-9** shows that the uptake of phosphate by PAA decreases markedly with increase in equilibrium pH. Since PAA in the free amine form was contacted with the phosphate test solutions, hydrogen ions transfer from H_3PO_4 and $H_2PO_4^-$ to RNH_2 to form the positive fixed site RNH_3^+ for the uptake of the resulting anions $H_2PO_4^-$ and HPO_4^{2-} onto the resin phase. Thus, PAA in free amine form simultaneously takes up hydrogen ion and the resulting anionic species as follows:

$$\overline{R\text{-}NH_2} + H_3PO_4 \rightleftharpoons \overline{R\text{-}NH_3^+ \cdot H_2PO_4^-} \tag{1}$$

$$\overline{R\text{-}NH_2} + Na^+ + H_2PO_4^- \rightleftharpoons \overline{R\text{-}NH_3^+ \cdot HPO_4^{2-} \cdot Na^+} \tag{2}$$

where, parentheses indicate the ion exchange resin phase. In Equation 2 the sodium ion enters into the resin phase to satisfy electroneutrality. Equations 1 and 2 suggest that the equilibrium pH of test solutions always increases from the initial pH of test solutions. For instance, when a test solution with the initial pH of 2.19 was equilibrated with PAA in the

free amine form, the pH increased to 3.09 at equilibrium. Then, reaction 1 is predominant below the equilibrium pH 4.7, because values of pKa_1, pKa_2 and pKa_3 for phosphoric acid are 2.16, 7.21 and 12.32, respectively (Ringbom, 1963). When the equilibrium pH of the test solutions is between 4.7 and 9.8, the predominant species in solution at equilibrium are $H_2PO_4^-$ and/or HPO_4^{2-} and the concentration of H_3PO_4 is substantially regarded as zero. Then, the predominant reaction is denoted by Equation 2 above an equilibrium pH = 4.7.

4.2.3.1.2. Effect of competing anions on uptake of phosphate

The selectivity sequence for typical univalent inorganic anions on strong-base anion exchange resins with crosslinked polystyrene matrices is: $ClO_4^- > I^- > NO_3^- > Br^- > Cl^- > H_2PO_4^-$ (Awual et al., 2008). So the effect of Cl^-, NO_3^- and ClO_4^- on phosphate uptake was tested in the presence of a fivefold molar concentration of each anion and the results are shown in **Figure 4-9** as a function of the equilibrium pH. Below pH 6, the uptake of phosphate is rather depressed by the three univalent anions and their interference becomes more marked with a decrease in pH. On the contrary, above pH 6 their interference is reduced and a marked difference is not observed indicating less interference by these univalent anions. These results mean that PAA prefers phosphate to these univalent anions, indicating the non-Hofmeister anion selectivity sequence for PAA. As anticipated by the concept of electroselectivity (Helfferich, 1962), SO_4^{2-} interfered more strongly with the uptake of phosphate than the univalent anions; with phosphate uptake depressed completely below pH 6, where the most dominant phosphate species is $H_2PO_4^-$. Between pH 7.2 and 12.3, the most dominant phosphate species becomes HPO_4^{2-}. However, the acid strength of HPO_4^{2-} is so weak that the following reaction (3) does not occur:

$$\overline{R\text{-}NH_2} + 2Na^+ + HPO_4^{2-} \rightleftharpoons \overline{R\text{-}NH_3^+ \cdot PO_4^{3-} \cdot 2Na^+} \qquad (3)$$

Then, uptake of phosphate as PO_4^{3-} is difficult above equilibrium pH 9.8. So the maximum uptake of phosphate is observed between pH 6 and 10 in the presence of sulfate. The species HPO_4^{2-} adsorbing according to Equation 2 is able to form a hydrogen bond with the protonated site RNH_3^+ as indicated from studies on "anion coordination chemistry" (Kimura et al., 1982a; Dietrich et al., 1981; Hosseini and Lehn, 1982). Then, the HPO_4^{2-}
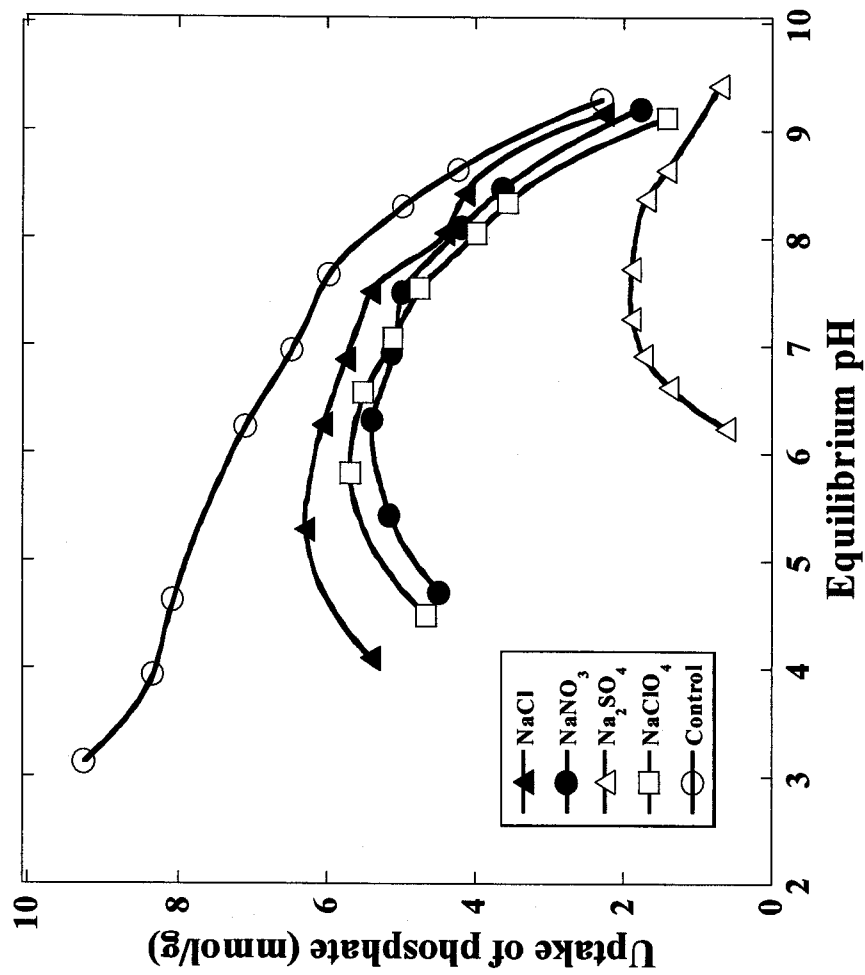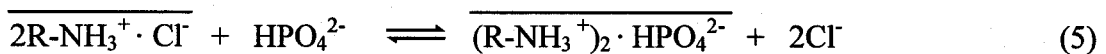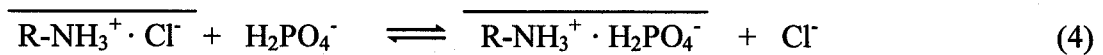
Figure 4-9- Uptake of phosphate as a function of equilibrium pH in the absence and presence of competing anions. PAA free amine form: 50 mg (dry weight). Solutions: 50 mL of 10 mM phosphate at various pH values without and with competing anion. Competing anion: 50 mM sodium salt of each anion. Equilibration: 30°C for 24 h. Control: without interfering anion.

species is more strongly adsorbed than SO_4^{2-} as shown from the pH-profile of phosphate uptake between pH 6 and 10 in the presence of SO_4^{2-}; (phosphate uptake 1.7 and 1.9 mmol/g at pH 6.9 and 7.7, respectively). These values are greater than a fifth of phosphate uptake at pH 6.9 and 7.7 in the absence of a competing anion. Consequently, the batch study concluded that PAA prefers phosphate species to the inorganic anions, which do not have a high basicity comparable to that of HPO_4^{2-}. On the other hand, there is no practical effect was observed by hybrid anion exchange adsorbent and metal loaded adsorbent (Wasay et al., 1996b; Zhao and Sengupta, 1998; Blaney et al., 2007; Zhu and Jyo, 2005) but their kinetic performance are not high enough at high feed flow rate.

4.2.3.2. Column-mode study

4.2.3.2.1. Effect of flow rate on uptake of phosphate

As discussed in the foregoing section, PAA shows the highest selectivity to phosphate around pH 7 which is approximately the pH of most lake and river waters. Thus, the pH of the feed in this column-mode study was fixed at 7.0 ± 0.1. Since PAA was used in hydrochloride form univalent and divalent phosphate species are adsorbed according to Equations 4 and 5, respectively.

$$\overline{R\text{-}NH_3^+ \cdot Cl^-} + H_2PO_4^- \rightleftharpoons \overline{R\text{-}NH_3^+ \cdot H_2PO_4^-} + Cl^- \tag{4}$$

$$\overline{2R\text{-}NH_3^+ \cdot Cl^-} + HPO_4^{2-} \rightleftharpoons \overline{(R\text{-}NH_3^+)_2 \cdot HPO_4^{2-}} + 2Cl^- \tag{5}$$

Since the amino group content of PAA is as large as 14.6 mmol/g, a high flow rate can be used providing the concentration of a target ion in the feed is not higher than 10 mM. So the effect of flow rate of the feed on phosphate uptake was tested by changing the feed flow rate from 300 to 2400 h^{-1} while the phosphate concentration of the feed was fixed at 1.0 mM. The effect of feed flow rate on phosphate breakthrough profiles is shown in **Figure 4-10** and indicates that the breakthrough points decrease markedly with increase in the feed flow rate. Since the column profiles after breakthrough do not have practical a meaning from the viewpoint of phosphate removal, the whole profile up to $C/C_0 = 1$ were not evaluated in this study and the volume of the feed supplied to the column was limited

to 1000 BV. Details of these experiments are given in **Table 4-5** (entry nos. 1 - 8) showing that with an increase in flow rate, breakthrough capacities and total uptake decrease markedly. Since the PAA resin diameter of 0.13 – 0.18 mm, phosphate uptake is diffusion controlled in the resin phase and only the functional groups near the particles surface can contribute to phosphate uptake up to the breakthrough points at high flow rates of the feed. Indeed, breakthrough capacities at flow rates of 300 and 2400 h^{-1} correspond to only ca. 20 and 11 % of the functional group content, respectively. Although the majority of the functional groups located in central part of the resin particles are not available to phosphate at a flow rate of 300 h^{-1}, the phosphate breakthrough capacity of PAA of 1.6 mmol/g at the flow rate of 2400 h^{-1} is attractive practically for phosphate removal. In addition to the non-Hofmeister anion selectivity behaviour, PAA can take up appreciable amounts of phosphate even at the high flow rate of 2400 h^{-1} because of its extremely high density of amino groups.

4.2.3.2.2. Effect of phosphate concentration in feeds on uptake of phosphate

The effect of feed phosphate concentration on phosphate uptake was tested over the range 0.50 - 4.06 mM phosphate (**Table 4-5** entry nos. 3, 4, and 9 – 14). **Figure 4-11** shows the breakthrough points and capacities as a function of C_0. Here, the quantity of phosphate supplied to the column was fixed at 2.0 mmol and the feed flow rate at 600 h^{-1}. With decreasing phosphate concentration in the feed, the total uptake of phosphate slightly decreases but breakthrough capacity decreases more markedly. Here, the breakthrough point was designated by the feed volume where the phosphate concentration in the column effluent is 1% of the phosphate concentration in the feed. Then, the criterion for the breakthrough point becomes stricter with a decrease in the phosphate concentration of the feeds. For instance, criteria for $C_0 = 4.0$ and 0.5 mM are 0.04 and 0.005 mM, respectively. Consequently, the breakthrough capacity is more sensitive to the phosphate concentration of the feed compared with total phosphate uptake, so long as the quantity of phosphate supplied to the column is constant.

4.2.3.2.3. Rapid phosphate removal from feed containing phosphate at trace concentration level

Because of the large capacity of PAA for uptake of phosphate, the behaviour of PAA in a column was investigated using feeds containing relatively high concentrations of 0.50 – 4.06 mM. Also of interest is the possibility of rapid removal of phosphate from water containing phosphate at ppm P level. To purify large volumes of water polluted with such a low concentration of phosphate, high flow rates are desirable. Thus, phosphate removal was examined using a solution containing phosphate as low as 1.1 ppm P. Here, the feed (15000 BV, 30 L) was supplied to the column at a flow of 3500 h^{-1} (7.0 L/h). **Figure 4-12** shows the breakthrough curve of phosphate uptake at an extremely high feed flow rate in neutral pH region. The results in **Table 4-5** (entry nos. 15 and 16) show breakthrough points for duplicated runs were ca. 5700 BV (11.4 L) and the breakthrough capacities were ca. 1.0 mmol/g. It took 1.6 h to remove phosphate from 11.4 L of water containing 1.1 ppm P to less than 0.011 ppm P, although in this case the test solution only contained phosphate.

4.2.3.2.4. Elution and repeated use of the column

The adsorbed phosphate was quantitatively eluted with 2 M HCl at a flow rate of 3.5 h^{-1}. Elution reactions can be written as follows (6), (7):

$$\overline{R\text{-}NH_3^+ \cdot H_2PO_4^-} + HCl \;\rightleftharpoons\; \overline{R\text{-}NH_3^+ \cdot Cl^-} + H_3PO_4 \tag{6}$$

$$\overline{2R\text{-}NH_3^+ \cdot HPO_4^{2-}} + 2HCl \;\rightleftharpoons\; \overline{2R\text{-}NH_3^+ \cdot Cl^-} + H_3PO_4 \tag{7}$$
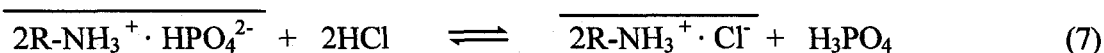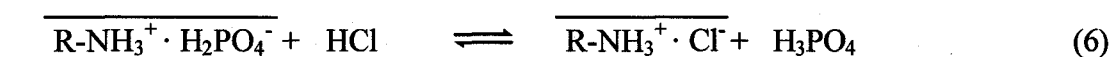
Figure 4-13 shows an example of the elution of adsorbed phosphate. Equations 6 and 7 show that during elution the PAA resin was simultaneously regenerated for the next phosphate adsorption operation. All results in the column study were obtained using the same column without replacement of PAA. Thus, this work suggests that PAA is a promising adsorbent for the rapid removal of phosphate from water.

Table 4-5- Detailed experimental conditions and summary of numerical data of column-mode study

| Entry no.	Feed				Breakthrough point (BV)	Breakthrough capacity (mmol/g)	Total uptake (mmol/g)	Amount eluted (mmol/g)	Recovery (%)
	solution pH	flow rate (h^{-1} in SV)	C_0 of phosphate (mM)	solution volume (BV)					
1	6.98	300	1.01	1000	597	3.12	5.06	5.55	109
2	6.98	300	1.01	1000	586	2.98	5.06	4.93	97.4
3	6.96	600	1.00	1000	540	2.79	4.87	5.27	108
4	6.96	600	1.00	1000	532	2.71	4.82	5.17	107
5	6.96	1200	0.99	1000	498	2.55	4.72	4.67	98.9
6	6.96	1200	0.99	1000	495	2.55	4.73	5.01	106
7	7.02	2400	0.98	1000	320	1.62	4.53	4.64	102
8	7.02	2400	0.98	1000	328	1.66	4.50	4.67	103
9	7.02	600	0.50	2000	1037	2.68	4.80	5.01	104
10	7.02	600	0.50	2000	1032	2.67	4.76	4.73	99.3
11	6.97	600	2.00	500	350	3.63	5.12	5.21	102
12	6.97	600	2.00	500	345	3.59	5.12	5.09	99.4
13	7.03	600	4.06	250	185	3.90	5.21	5.53	106
14	7.03	600	4.06	250	186	3.92	5.21	5.30	102
15	7.05	3500	0.035	15000	5700	1.03	2.58	2.57	99.6
16	7.02	3500	0.033	15000	5650	0.97	2.42	2.47	102

Resin bed volume: 2.0 mL
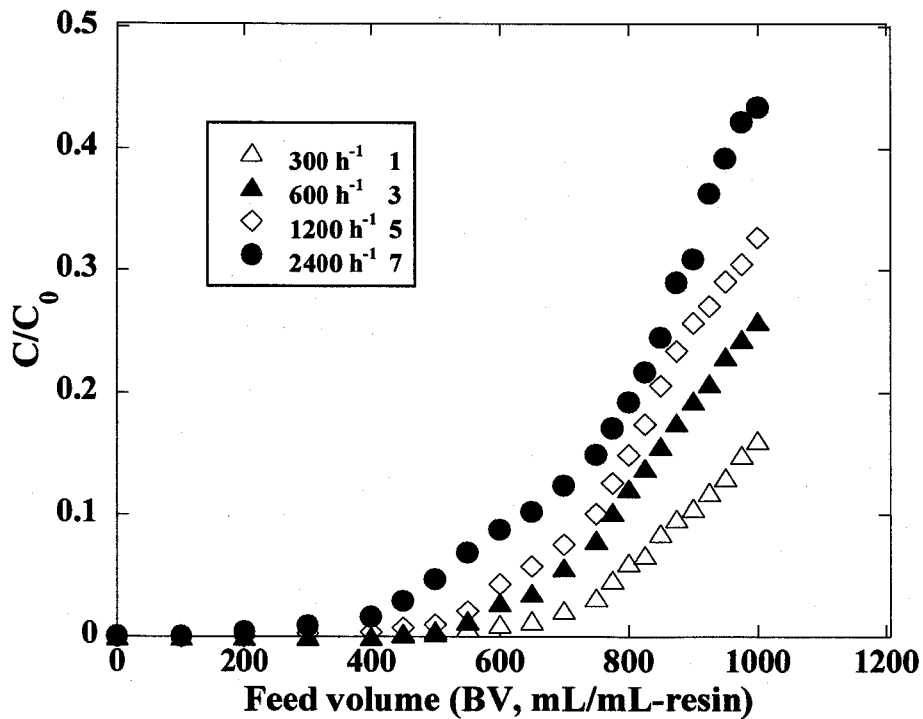
Figure 4-10- Dependence of breakthrough profiles of phosphate on flow rate of feed. Figure for each profile represents the run number in Table 4-5. Column: PAA in hydrochloride form (2.0 mL (wet), 0.38 g (dry). Feed: 1.0 mM phosphate at pH 7. Detailed conditions and results are given in Table 4-5.
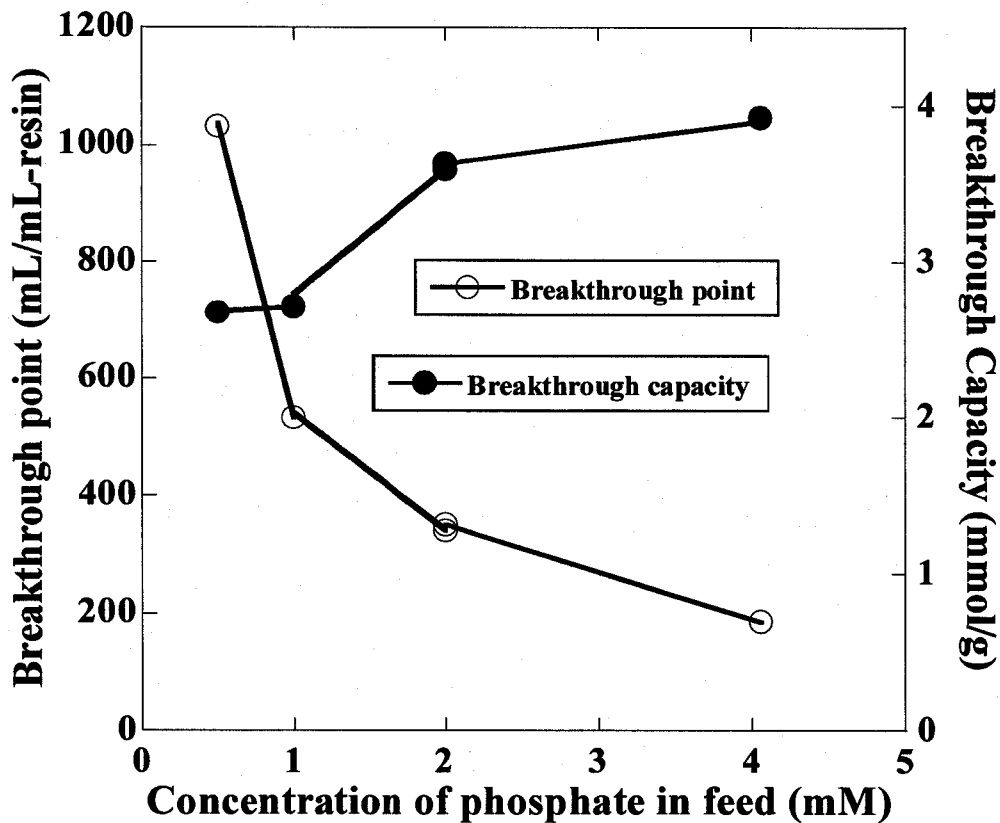

Figure 4-11- Effect of feed concentrations on phosphate uptake by PAA. For detailed conditions and results refer to entry nos. 3, 4 and 9-14 in Table 4-5.
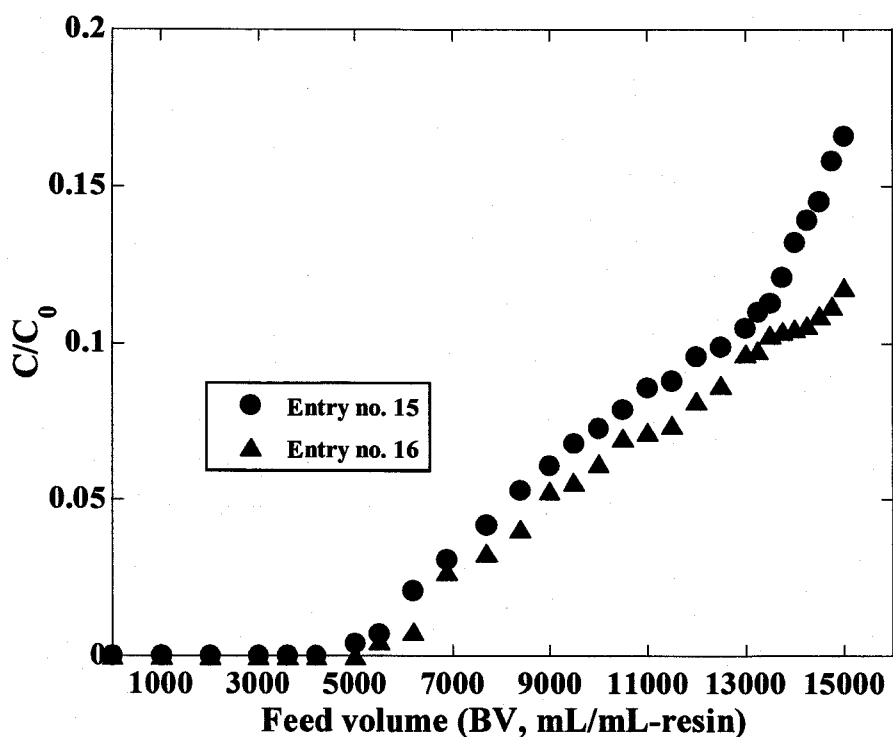
Figure 4-12- Uptake of phosphate by PAA packed column at high feed flow rate of 3500 h^{-1}. For detailed conditions and results refer to entry nos. 15 and 16 in Table 4-5.
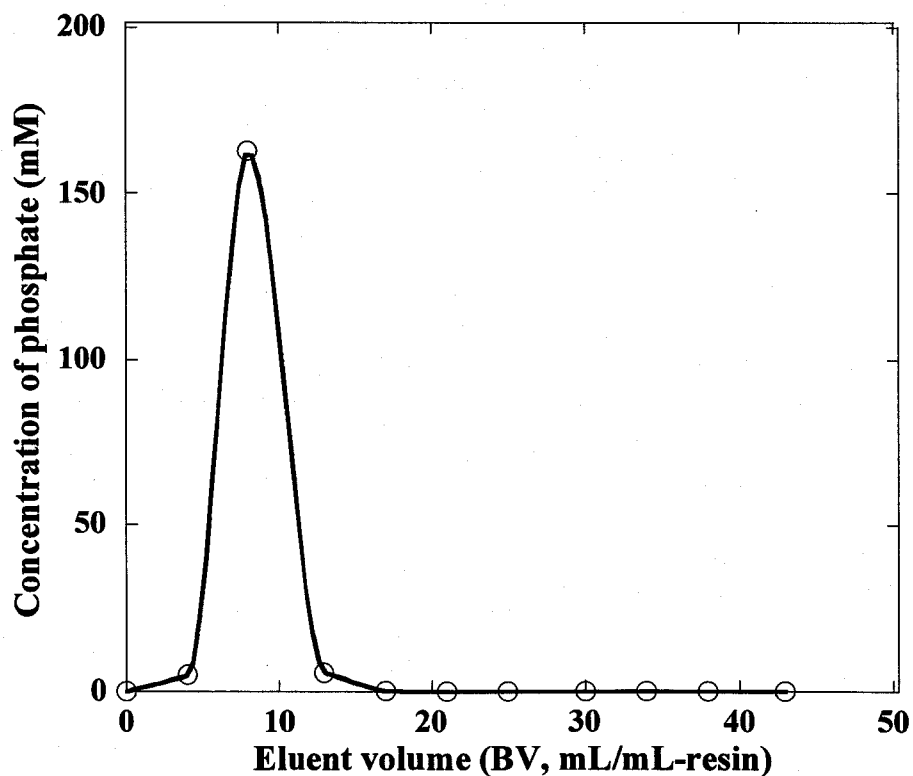

Figure 4-13- Elution of phosphate adsorbed on the PAA packed column. Eluent: 2 M HCl, flow rate: 3.5 h^{-1}. For other conditions refer to entry no. 16 in Table 4-5.

4.2.4. Conclusions

Batch-mode study revealed that PAA exhibits a non-Hofmesiter anion selectivity sequence and high equilibrium capacities of 2.3 − 9.2 mmol of P/g depending on pH. This comes from the high hydrophilicity of PAA because it is a weakly crosslinked polyallylamine, having an extremely high primary amine content of 14.6 mmol/g. Because of its non-Hofmeister behaviour, interference of chloride, nitrate, and perchlorate on uptake of phosphate is minimal and even sulfate does not strongly interfere with uptake of phosphate in contrast to strong-base anion exchange resins. Because of the extremely high content of the functional groups, PAA exhibits breakthrough capacities as high as 1- 2.6 mmol of P/g at the high flow rate of 1200 − 3500 h^{-1}. In addition, PAA can rapidly purify a dilute solution of phosphate as low as 1.1 ppm P. As future work, we would like to apply PAA resin to the rapid removal of arsenate and conduct detailed study on dependence of breakthrough capacities for phosphate on several factors, such as resin bed dimensions and beads sizes and so on.

ABSTRACT

Arsenate removal from water is necessary to control the drinking water quality, and phosphate removal from water is an essential to prevent eutrophication. This thesis describes results of detailed study on "development of arsenate and phosphate selective adsorbents having high kinetic performances" and consists of four chapters.

Chapter one reviews problems concerning on arsenate and phosphate and recent trends on development of new techniques for removal of both species.

Chapter two describes the preparation of a weak-base anion exchange fiber FVA and its application for selective removal of arsenate and phosphate from water. FVA was prepared by electron irradiation induced liquid phase graft polymerization of N-vinylformamide onto polyolefin fibers and by the subsequent alkaline hydrolysis of amide group on the grafted polymer chains. Two types of FVA were prepared: non-woven cloth type (FVA-c) for the batch-mode study and filamentary type (FVA-f) for the column-mode study. Batch-mode study clarified that FVA-c prefers arsenate and phosphate to chloride and sulfate in neutral pH region opposed to a commercially available strong-base anion exchange resin. Column-mode work clarified that FVA-f took up arsenate species from neutral pH solutions containing 1.0 - 99 mg of As/L at high feed flow rates of 100 - 1050 h^{-1} in space velocity. FVA-f also showed nearly the same performances in column-mode uptake of phosphate. Arsenate and phosphate adsorbed on FVA-f were quantitatively eluted with 1 M hydrochloric acid. During the elution operation, FVA-f was simultaneously regenerated into hydrochloride form for the next adsorption operation after rinsing with water.

Chapter three describes the preparation of Zr(IV) loaded ligand exchange adsorbents based on phosphonate/sufonate bifunctional resin and fiber and their performances in removal of arsenate and phosphate from water. First, the removal of arsenate and phosphate from water by Zr(IV) loaded phosphonate/sulfonate bifunctional resin named "monophosphonic acid resin" was studied. This ligand exchange resin exhibited the high selectivity to arsenate or phosphate over competing anions. Sodium salts of chloride, nitrate and sulfate did not interfere with uptake of arsenate or phosphate but they slightly enhanced uptake of arsenate and phosphate. Adsorbed arsenate and phosphate were quantitatively eluted with aqueous sodium hydroxide. Second, ligand exchange fibrous

adsorbent was prepared by loading Zr(IV) onto a bifunctional cation exchange fiber containing both phosphonate and sulfonate in order to improve kinetic performances, since granular resin based ligand exchanger was not excellent in kinetic performances. The bifunctional cation exchange fiber was prepared by phosphorylation and sulfonation of the precursory fiber, which was obtained by co-graft polymerization of chloromethylstyrene and styrene onto polyethylene coated polypropylene fiber. Performances of the Zr(IV) loaded fiber as arsenate and phosphate adsorbent were studied in column-mode method. The column packed with Zr(IV) loaded fiber removed arsenate from a weakly acidic pH solution containing 0.016 mM arsenate (1.2 mg of As/L) even at a flow rate of 200 h^{-1}. On the other hand, Zr(IV) loaded adsorbent was able to remove phosphate from a feed solution containing 0.216 mg of P/L and three different competing anions (chloride, bicarbonate and sulfate) at a flow rate of 250 h^{-1}. The fibrous ligand exchanger exhibited excellent kinetic performances than the granular resin one.

Chapter four describes the removal of arsenate and phosphate by a crosslinked polyallylamine resin PAA. PAA exhibits a non-Hofmeister anion selectivity sequence of arsenate or phosphate > sulfate > nitrate ≈ perchlorate > chloride, and it takes up high amount of arsenate or phosphate. Characteristic anion selectivity and high capacities of PAA for arsenate or phosphate come from its extremely high primary amino group content of 14.6 mmol/g, which give high hydrophilicity to the resin. Therefore, chloride and sulfate did not markedly interfere with uptake of arsenate and phosphate even in their presence of fivefold molar concentration of target species. In addition, this work clarified that PAA exhibits breakthrough capacities for arsenate or phosphate as high as 0.8 – 3.5 mmol/g in column-mode under high flow rates of 250 – 4000 h^{-1}.

This study has shown that FVA, Zr(IV) loaded phosphonate/sulfonate binfunctional fiber and PAA are highly effective new adsorbents for arsenate and phosphate removal with high kinetic performances.

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