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Rapid removal of arsenate and phosphate from water by highly selective anion exchange adsorbents

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Abstract—Arsenate (As(V)) removal from water is necessary to control the drinking water quality, and phosphate removal from water is an essential to prevent eutrophication. We prepared a weak-base anion exchange fiber FVA and its application was observed for selective removal of As(V) 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. The removal of As(V) and phosphate by a crosslinked polyallylamine resin PAA also studied. PAA exhibits a non-Hofmeister anion selectivity sequence of As(V) or phosphate > sulfate > nitrate > chloride, and it takes up high amount of As(V) or phosphate. Characteristic anion selectivity and high capacities of PAA for As(V) or phosphate come from its extremely high primary amino group content of 14.6 mmol/g, which give high hydrophilicity to the resin phase.

INTRODUCTION

It is prominent that As(V) and phosphate are hazardous anions for human being as well as environment. Arsenic (As) contamination of groundwater has been called the largest 20th - 21st century mass poisoning calamity in human history [1], [2]. Millions of people in the world and More than 70 million people in Bangladesh are adversely affected by arsenic contaminated water [1]. 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 sub-ppm [2]. A new maximum contamination level is permitting the presence of low arsenic in drinking at 10 ppb [3]. Eutrophication is considered as one of the most important environmental problems and phosphate is one of key compounds responsible for eutrophication. Therefore, the concentration of phosphate in water is limited to below 10 ppb phosphorus (P) to escape from eutrophication problems [4]. Thus removal of As(V) and phosphate from water is very important to save human beings, plants and animals. Several technologies were proposed to purification of water contaminated with As and P and their adsorption rates are not so rapid. Among them, ion exchange processes are attractive for As and P removal because repeated use of ion exchangers is possible [5]. Then these works were planned for rapid remediation of contaminated water and environment.

Commercially available anion exchange resins are crosslinked polystyrene having chemically fixed quaternary ammonium groups or amino groups, do not have the high selectivity to As(V) and phosphate over Cl⁻, HCO₃⁻ and SO₄²⁻ because of high hydrophobic nature and they prefer less hydrated anions to highly hydrated counterions so long

as counterions have the equal charge number [6]. In this article, weak-base anion exchanger (FVA) and crosslinked polyallylamine (PAA) resin is rare organic exchanger, which can take up As(V) and phosphate in the presence of competing anions such Cl⁻ and SO₄²⁻ at high feed flow rate even 4000 h⁻¹ in space velocity.

MATERIAL AND METHOD

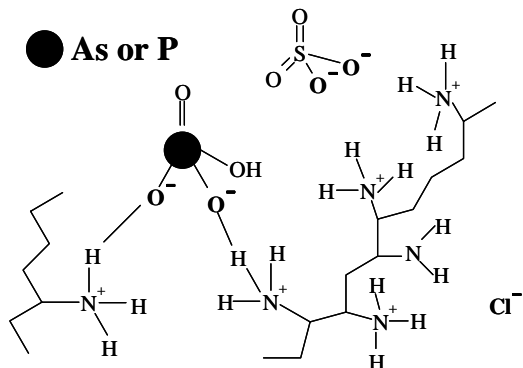
The structure of FVA and PAA is shown elsewhere [5], [7]. All chemicals used were guaranteed grade unless otherwise specified. Preparation of FVA was reported in detail elsewhere [5]. PAA was developed as reagent for research works. Nitrogen content of FVA and PAA (both in free amine form) are 7.3 mmol/g and 14.6 mmol/g, respectively. The breakthrough point is designated as the feed volume in bed volume (BV) supplied to a column up to C/C₀ = 0.01. Here, C₀ and C represent concentrations of As(V) or phosphate in feeds and in the column effluents, respectively. The volume of the wet FVA and PAA 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/resin bed in mL. The preparation of FVA and PAA column and related procedure are described elsewhere [5], [7].

DISCUSSION

To clarify effect of pH on uptake of As(V) and phosphate by FVA and PAA, feed solutions with different pH values from 2.0 to 7.0 were fed to the column at a given flow rate. FVA and PAA worked well within the tested pH range and low pH was preferable [5], [8].

Flow rates of feeds in As(V) and phosphate removal by metal loaded ligand exchange and metal oxides based adsorbents were usually from 10 to 40 h⁻¹. Here one example stated of PAA. The functional group content of PAA is extremely high (14.6 mmol/g), it is expected that high feed flow rates will be usable for adsorption operation of As(V) or phosphate. Then, the flow rate effect on breakthrough capacity for As(V) was investigated changing the feed flow rate from 250 to 2000 h⁻¹. The breakthrough capacity decreased markedly with an increase in the feed flow rate. Flow rate at 250 h⁻¹, the breakthrough capacity was 3.53 mmol/g. 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 [7].

Main anions to be associated with arsenic and phosphate in groundwater are Cl^- , HCO_3^- , SO_4^{2-} and in some cases NO_3^- . Then, their effect on uptake of As(V) and phosphate was tested using feeds containing Cl^- , NO_3^- or SO_4^{2-} as interferent anion by both FVA and PAA. Interference of equimolar Cl^- or NO_3^- is not marked, but SO_4^{2-} more markedly interferes with uptake of As(V) and phosphate by FVA and PAA as reported [5], [7], [8]. The basicity of divalent As(V) or phosphate anion is much higher than that of SO_4^{2-} , divalent As(V)/phosphate 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 1.



Scheme 1- Schematic illustration for the high selectivity of protonated FVA or PAA to arsenate or phosphate.

To purify huge volume water contaminated with trace As(V) and phosphate by column-mode method, the adsorbent should have kinetically excellent performances. The high feed flow rate shortens the time required for purification. In FVA column, phosphate removal was tested supplying feeds containing 0.021 mM (0.65 ppm as P) phosphate to the column at a flow rate of 2500 h⁻¹. The breakthrough point was 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 [9]. The arsenic concentration in water in Ganges delta areas is usually 0.5 through 3.0 mg/L. Then, 0.020 mM As(V) (1.52 mg of As/L) was supplied to the PAA column at a flow rate of 4000 h⁻¹ (9.6 L/h). Fig. 1 shows breakthrough curves of As(V). The breakthrough point is 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 As(V) 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 As(V), although ca. 6% of functional groups were active to take up of As(V) at the high feed flow rate of 4000 h⁻¹. The high kinetic performance is possible because hydrogen bonding and ion exchange are much faster than ligand exchange complexation reaction mechanism.

The adsorbed As(V) and phosphate from FVA and PAA was able to be quantitatively eluted with 1-2 M HCl. During the elution procedure, FVA and PAA in the column are simultaneously regenerated into the initial polyammonium form. Then, the FVA and PAA packed

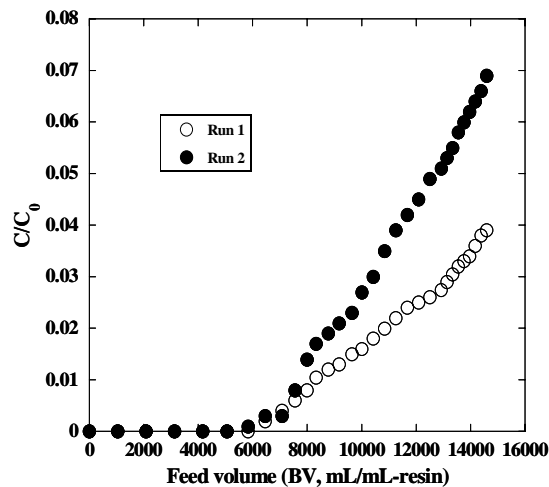


Fig. 1. Breakthrough profile of arsenate in its column-mode uptake by PAA from a 0.020 mM arsenate feed at feed flow rate of 4000 h⁻¹.

column can be used in the next adsorption operation after washing the column with water.

CONCLUSION

Both FVA and PAA exhibit a non-Hofmeister anion selectivity sequence and high breakthrough capacities depending on pH of feeds. These come from the high hydrophilicity of FVA & PAA because weakly crosslinked polyamine or polyallylamine. Because of its non-Hofmeister behaviour, interference of Cl^- , HCO_3^- and NO_3^- on uptake of As(V) or phosphate is minimal and even SO_4^{2-} does not strongly interfere with uptake of As(V) or phosphate.

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