



# The retention profile of phosphate ions in aqueous media onto ion pairing immobilized polyurethane foam: Kinetics, sorption and chromatographic separation

A.S. Bashammakh

Department of Chemistry, Faculty of Science, King Abdulaziz University, P. O. Box 80203, Jeddah 21589, Kingdom of Saudi Arabia

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## ABSTRACT

A strategy for enriching, separating and determining the inorganic phosphate ions in water based on the use of polyurethane foam (PUFs) physically immobilized with some ion pairing or basic dyes has been reported. The retention of inorganic phosphate from the test aqueous solution containing molybdate ions onto untreated- and ion pairing reagent e.g. crystal violet (CV) or tetrabutylammoniumtetrafluoroborate ( $\text{Bu}_4\text{N}^+\cdot\text{BF}_4^-$ ) impregnated PUFs solid phase extractor was followed the order: unloaded  $< \text{CV} < \text{Bu}_4\text{N}^+\cdot\text{BF}_4^-$  treated PUFs sorbent at pH 3.5–4.5. The kinetics of analyte sorption onto  $\text{Bu}_4\text{N}^+\cdot\text{BF}_4^-$  treated PUFs at optimized pH (pH 3.4–4.5) was fast and followed first order rate equation with an overall rate constant of  $0.062 \text{ min}^{-1}$ . Film and intraparticle transport are the main factors controlling the rate of phosphate sorption onto the sorbent from solutions at pH = 3.5–4.5. Phosphate uptake followed Langmuir and Freundlich isotherm models. Thus, a dual-mode sorption involving absorption related to “weak base anion exchanger” and an added component for “surface adsorption” is the most probable retention mechanism for phosphate uptake by  $\text{Bu}_4\text{N}^+\cdot\text{BF}_4^-$  loaded PUFs sorbent. Chromatographic separation of phosphate by  $\text{Bu}_4\text{N}^+\cdot\text{BF}_4^-$  treated PUFs packed column was carried out. The number (N) and the height equivalent to the theoretical plates (HETP), critical and breakthrough capacities were found equal  $81 \pm 4$ ,  $0.13 \pm 0.02 \text{ mm}$ ,  $2.5 \pm 0.2$  and  $27.25 \pm 2.06 \text{ mg g}^{-1}$ , respectively. These results suggested the use of the proposed  $\text{Bu}_4\text{N}^+\cdot\text{BF}_4^-$  treated PUFs in packed column for separation of trace levels of phosphate in water. The retained phosphate were recovered quantitatively ( $102.6 \pm 2.4$ – $106.2 \pm 3.2\%$ ) with NaOH ( $0.5 \text{ mol L}^{-1}$ ) and analyzed. The proposed column was applied for separation and recovery of phosphate ions in waste- and seawater samples. The results were in good agreement with the spiked and expected phosphate concentrations at 95% confidence.

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## 1. Introduction

Removal of phosphate and heavy metal ions from wastewater by chemical methods e.g. solid phase extractor (SPE) and biological treatment has been widely investigated [1–22]. Phosphorus concentrations are below limit of detection (LOD) over much of surface water oceans. The challenge for analytical chemists is to reduce the LOD to enable the detection and measuring phosphate in seawater. Dissolved inorganic nutrient such phosphate (DIP) and nitrogen (DIN) are the most desirable species to the phytoplankton due to re-mineralize the organic species of the nutrients which requires various enzyme actions [1,23].

Current abatement and remediation of phosphorus in wastewater can be simply classified as: chemical precipitation, sorption by suitable adsorbents and biological removal [24–42]. Adsorption of phosphate

on solid phase extraction via the formation of ion associates with Malachite Green, Crystal violet, Rhodamine 6G and Rhodamine B in the presence of molybdate has been reported [43]. A pretreatment of refined aspen wood fiber with an aqueous solution of a non-toxic anionic polymer such as carboxy methyl cellulose (CMC) for (ortho) phosphate removal has been reported [44]. Phosphoric acid resin RGP immobilized with zirconium(IV) has been used for phosphate removal [45].

Polyurethane foams (PUFs) have been used as an excellent support in reversed phase extraction chromatography, gas-solid and gas-liquid partition chromatography [46]. PUFs in both foamed and microspherical forms have excellent capacity for firmly retaining various loading and extracting agents [46–49]. PUFs are effective solid phase extractor enough for metal speciation in waters. Thus, the present article is focused on: i) Studying the retention profile of phosphate from aqueous molybdate media onto reagent treated PUFs treated ion pairing reagent; ii) kinetics and sorption characteristics of phosphate uptake by PUFs sorbent and finally iii) application of  $\text{Bu}_4\text{N}^+\cdot\text{BF}_4^-$  treated PUFs packed column for separation and subsequent determination of phosphate in water.

E-mail address: [abashammakh@kau.edu.sa](mailto:abashammakh@kau.edu.sa).

## 2. Experimental

### 2.1. Apparatus

A single beam Digital Spectro UV-VIS RS Labomed Inc. spectrophotometer with glass and quartz cells (10 mm path length) was used for measuring the absorbance. A Soxhlet extractor and a pH meter model 3305 (JENWAY) were used for foam purification and pH measurements, respectively. A corporation precision scientific mechanical shaker (Chicago, CH, USA) with a shaking rate in the range 10–250 rpm and glass columns (18 cm × 15 mm i.d.) were used in batch and flow experiments, respectively. A Milli-Q Waters Plus system (Milford, MA, USA) was used for water supply.

### 2.2. Reagents and materials

All chemicals used were of analytical reagent grade. Aqueous solutions were prepared with ultra-pure water from a Milli-Q unit (Millipore, Milford, MA, USA). A stock solution of  $\text{NH}_4\text{H}_2\text{PO}_4$  (Merck, Darmstadt, Germany) ( $1.0 \text{ mg mL}^{-1}$ ) was prepared in doubly distilled water (250 mL). A series of standard phosphate solutions were freshly prepared by dilution as required daily. Stock solutions of crystal violet (CV) and  $\text{Bu}_4\text{N}^+ \cdot \text{BF}_4^-$  and were purchased from BDH (Poole, England). CV,  $\text{Bu}_4\text{N}^+ \cdot \text{BF}_4^-$  (0.1% w/v) and ammonium molybdate (Fluka AG, Switzerland) (2.0% m/v) were prepared by dissolving the required weight individually in doubly distilled water. Commercial white sheets of open cell polyether type based PUFs were used. Foam cubes of (10–15 mm edge) were cut from the foam sheets, washed and dried as reported [48,49]. A series of Britton Robinson (B-R) buffer of pH 2–11 was prepared as reported [50]. Low density polyethylene (LDPE) bottles were carefully cleaned with hot detergent, soaked in 50% HCl (BDH),  $\text{HNO}_3$  ( $2.0 \text{ mol L}^{-1}$ ), subsequently washed with dilute HCl ( $0.5 \text{ mol L}^{-1}$ ) and finally rinsed with deionized water. The CV or reagent  $\text{Bu}_4\text{N}^+ \cdot \text{BF}_4^-$  (1.0% w/v) was dissolved in water, shaken with PUFs cubes with efficient stirring for 30 min, squeezed and finally dried [49,51].

### 2.3. Recommended procedures

#### 2.3.1. Batch experiments

In dry and clean LDPE bottles, the test aqueous solutions of phosphate ( $100 \text{ mL}$ ,  $10 \mu\text{g mL}^{-1}$ ) in the presence of ammonium molybdate (0.1%) solution at pH 3.5–4.5 adjusted with few drops of  $\text{HNO}_3$  ( $0.3 \text{ mol L}^{-1}$ ) and/or  $\text{NH}_4\text{OH}$  ( $3.0 \text{ mol L}^{-1}$ ) were shaken with accurate weights ( $0.2 \pm 0.01 \text{ g}$ ) of the untreated- and ion pairing reagent CV or  $\text{Bu}_4\text{N}^+ \cdot \text{BF}_4^-$  loaded PUFs cubes on a mechanical shaker for 120 min. The aqueous phase was separated out and the amount of phosphate remained in the aqueous phase was measured by the molybdenum blue method at  $830 \text{ nm}$  [50]. The amount of phosphate retained onto PUFs cubes was then calculated from the difference ( $A_b - A_a$ ) between the absorbance of phosphate solutions before ( $A_b$ ) and after ( $A_a$ ) extraction. The extraction percentage (% E) and the distribution ratio (D) of phosphate uptake on the sorbents were then calculated [51].

Similarly, the interference of commonly associated ions  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  at 10–1000 fold excess on the phosphate ( $10.0 \mu\text{g mL}^{-1}$ ,  $100 \text{ mL}$ ) uptake from the test aqueous molybdate solution was also studied. Phosphate ions retained onto  $\text{Bu}_4\text{N}^+ \cdot \text{BF}_4^-$  treated PUFs were determined [50].

#### 2.3.2. Chromatographic separation of phosphate onto $\text{Bu}_4\text{N}^+ \cdot \text{BF}_4^-$ treated PUFs packed column

Quantitative retention and elution of phosphate on the reagent loaded PUFs ( $2 \pm 0.01 \text{ g}$ ) packed column were carried out as follows: Tap or distilled water (1.0 L) samples adjusted to pH 4 in the presence of molybdate ions was spiked with various concentrations of phosphate ( $0.01$ – $2 \mu\text{g mL}^{-1}$ ) were percolated at  $5.0 \text{ mL min}^{-1}$  flow rate through

the PUFs packed column. The retained phosphate species was quantitatively recovered from the reagent foam packed column by percolating NaOH ( $10 \text{ mL}$ ,  $0.5 \text{ mol L}^{-1}$ ) at  $2 \text{ mL min}^{-1}$  flow rate. A blank experiment under the same experimental conditions of flow rate and reagent was recorded. Phosphate content before and after percolation through the PUFs in the effluent and after elution was measured at  $830 \text{ nm}$  [50].

### 2.4. Analytical applications

The analytical utility of the proposed method for the preconcentration of phosphate ions in water samples was investigated. Environmental water samples e.g. waste- and seawater samples (1.0 L) were collected and filtered through a  $0.45 \mu\text{m}$  membrane filter (Milex, Millipore Corporation). The test phosphate solution in the presence of molybdate (0.1% m/v) before and after spiking with various amounts of phosphate ( $0.5$ – $20 \mu\text{g}$ ) was percolated through  $\text{Bu}_4\text{N}^+ \cdot \text{BF}_4^-$  treated PUFs at  $5.0 \text{ mL min}^{-1}$ . The retained phosphate species on the sorbent was recovered from the sorbent packed column by elution with NaOH ( $10 \text{ mL}$ ,  $0.5 \text{ mol L}^{-1}$ ) at  $2 \text{ mL min}^{-1}$  flow rate. A blank experiment was carried out under the same experimental conditions of flow rate and reagent. Phosphate content before and after percolation through the treated PUFs in the effluent and after elution was measured at  $830 \text{ nm}$  [50].

## 3. Results and discussion

### 3.1. Retention profile of phosphate by untreated and treated PUFs

Recently, considerable progress has been made on the use of PUFs as an inexpensive and effective solid sorbent for the removal of water pollutants [46–49]. PUFs sorbent concentrate inorganic and organic substances from different aqueous media by the phase distribution mechanism rather than adsorption [46–49]. Preliminary study has shown no considerable extraction (<10%) of phosphate ions from the aqueous media by the unloaded PUFs, CV and  $\text{Bu}_4\text{N}^+ \cdot \text{BF}_4^-$  loaded PUFs at various time intervals. Thus, the extraction of the phosphate was carried out from aqueous media in the presence of molybdate ions by the used of solid sorbents. The retention of phosphate by the solid PUFs sorbent followed the order:  $\text{Bu}_4\text{N}^+ \cdot \text{BF}_4^-$  loaded PUFs > CV-loaded PUFs > untreated PUF. Representative results are demonstrated in Fig. 1. Maximum retention was achieved after 60, 75 and 90 min shaking time, respectively. Thus, polyurethane foams physically treated with  $\text{Bu}_4\text{N}^+ \cdot \text{BF}_4^-$  was used in the subsequent work.

The probable reaction between phosphate ions and molybdate to form 12-molybdophosphoric acid anion can be expressed by the following equation [43]:

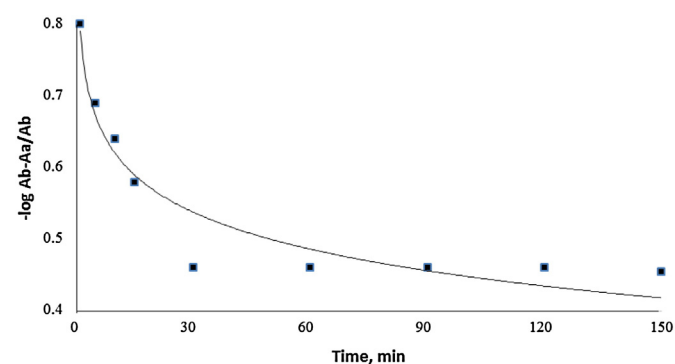


Fig. 1. Rate of phosphate ( $10.0 \mu\text{g mL}^{-1}$ ) sorption from aqueous ammonium molybdate (0.1% m/v) onto  $(\text{Bu}_4\text{N}^+ \cdot \text{BF}_4^-)$ -loaded PUF (0.1 g) at  $25 \pm 0.1 \text{ }^\circ\text{C}$ .

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