



# Effects of pH, soluble organic materials, and hydraulic loading rates on orthophosphate recovery from organic wastes using ion exchange

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## ARTICLE INFO

### Article history:

Received 19 June 2018

Received in revised form

17 January 2019

Accepted 19 January 2019

Available online 23 January 2019

### Keywords:

Resource recovery

Organic waste

Nutrient reuse

Orthophosphate

Ion exchange

Anaerobic digestion

## ABSTRACT

Phosphorus recovery from organic wastes attracts more and more attentions because of the phosphorus sustainability challenges. Ion exchange (IX) was used in this study to recover orthophosphate (ortho-P) from the anaerobic digester (ADs) supernatant of an organic waste. The effects of pH, soluble organic materials (SOM), and hydraulic loading rates (HLR) on phosphate recovery were investigated by column tests. The results of tests with model water showed that the IX capacities were 64.2 mg P/g and 36.7 mg P/g at pH of 4.5 and 9.0, respectively. The desired HLR of ortho-P capture was 0.69 m/H (3 BV/h), with ortho-P capture efficiency and recovery efficiency of about 90% and 80%, respectively. The ortho-P desorption efficiencies with NaOH and KNO<sub>3</sub> brines as eluents were investigated, finding that both NaOH and KNO<sub>3</sub> could be substitutions of officially recommended NaCl to reduce the harmful effect on soil or plants in applications. The results of tests with ADs supernatant showed that the ortho-P capture capacity decreased to 14.3 mg P/g, with great disruption of SOM. Both ortho-P and SOM were desorbed well with over 85% ortho-P recovery efficiency and no detrimental effect on resin reuse. Regenerate with KNO<sub>3</sub> could create mobile nutrients solution containing a N/ortho-P/K mass ratio of 17:8:75, which could balance deficient fertilizer. This research promotes the current understanding of phosphate recovery from organic wastes for fertilizer application.

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## 1. Introduction

Phosphorus is crucial for the development of plants and animals as well as for industrial manufactures because of the worldwide need for agricultural fertilizer (Wollmann et al., 2018). The world's economically useful phosphorus is “phosphate rock”, which is a non-renewable and non-substitutable natural resource (Chen and Graedel, 2015; Syers et al., 2011). Growing concerns exist regarding phosphate sustainability challenges (phosphate runoff, eutrophication and uncertainty about phosphate supplies) (Childers et al., 2011; Huang et al., 2017; Wyant et al., 2013). However, the wide use of phosphorus inevitably results in large amounts of orthophosphate (ortho-P) bearing wastes (Podstawczyk et al., 2017). Thus, technologies are needed to recovery and reuse of ortho-P (Rittmann et al., 2011).

Numerous organic waste (OW) streams from wastewater bio treatment plants, such as livestock manure, poultry manure, microbial biofuel residual, and waste activated sludge (WAS) are regarded as potential ortho-P reservoirs with high concentrations of phosphate (Gifford et al., 2015; Huacheng et al., 2012; Xu et al., 2018). For example, the phosphate concentrations in an anaerobic fermentation supernatant are as high as 500 mg P/L (Cornel and Schaum, 2009). Influence factors of ion exchange (IX) technology were intended to capture ortho-P from anaerobically digested waste streams and produce liquid concentrates containing high levels of ortho-P that can be used as nutrient fertilizers for agriculture. In this way, highly concentrated “mobile recovery nutrients” could be repurposed for beneficial use large distances away.

The physical and chemical characteristics of ortho-P and effectively IX technology led researchers to connect strong-base anionic (SBAX) resin. It has been successfully used for the removal of anions such as uranium (Stucker et al., 2011) and arsenate (Athanasaki et al., 2015). But few literature used it for phosphate recovery (Awual and Jyo, 2011; Chen et al., 2002). Meanwhile, successful regeneration allows continued use of the SBAX resin (Gifford et al.,

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2015). However, major differences exist between the design and operating conditions that meet effluent ortho-P goals and the conditions intended to maximize ortho-P recovery in IX. These conditions include influent solution pH, influent ortho-P concentration, hydraulic loading rate (HLR) onto IX contactors and eluent choice.

Monobasic phosphate ( $\text{H}_2\text{PO}_4^-$ ) and dibasic phosphate ( $\text{HPO}_4^{2-}$ ) anions always coexist in water bodies, wastewaters, as well as anaerobic fermentation liquids. The pH of natural water and municipal wastewater normally ranges from 6.5 to 7.3, so  $\text{H}_2\text{PO}_4^-$  is the main phosphate specie (Sawyer et al., 1978). However, the anaerobic fermentation of OW could be controlled at an acidogenic fermentation stage with a pH as low as 5.0 (Noike et al., 1985), and  $\text{HPO}_4^{2-}$  would be dominant. These anions have different ortho-P exchange capacities because of differences in the charge equivalency and selectivity of IX resins towards each ion (Xie et al., 2014; Yang et al., 2014). Influent solution pH influences ortho-P speciation. Ortho-P has pKa values of 2.1, 7.2, and 12.7. Therefore, experiments were conducted across a range of pH conditions.

Many studies on ortho-P recovery using IX were performed with synthetic wastewater containing low ortho-P concentrations in the range of 0.26–30 mg P/L (Blaney et al., 2007; Nur et al., 2014; Sarkar et al., 2011; Sengupta and Pandit, 2011). In contrast, the supernatant from anaerobic digesters (ADs) contains 100 to over 500 mg P/L (Cornel and Schaum, 2009). Fermentation in ADs not only converts much of the cellular and other organic phosphate to ortho-P, but it also results in high concentrations of soluble organic material (SOM) (Hagos et al., 2017; Wang et al., 2014). SOM can potentially compete with ortho-P ions for IX exchange sites. It is unique that ortho-P recovery was explored using IX from ADs supernatant containing ortho-P and SOM.

HLR influence IX performance and are usually selected to minimize reactor size during water treatment applications. These rates also rely upon blending treated water effluents from multiple IX contactors to meet regulated effluent ortho-P limits. Loading rates influence the shape and length of the mass transfer zone in IX contactors, which influences the bed depth. In order to maximize ortho-P loading, without any ortho-P breakthrough, the impact of HLR on ortho-P capture was investigated by IX resins.

Regeneration of spent IX resins is usually accomplished using NaCl brine and loading rates designed to effectively replace anions on the resin with chloride ions. That is to maximize the concentration of P in the regeneration stream containing anions and cations. In practice, at full-scale ion exchange plants, a highly concentrated NaCl solution (3–12%) is commonly used for the regeneration of SBAX resin (Clifford et al., 2011). There are recognized disadvantages associated with a high concentration of NaCl in the eluent as “mobile nutrient”, which is detrimental to biological processes of soil or plants in land application (Cañedo-Argüelles et al., 2013; Panswad and Anan, 1999). Other cations, brine concentrations, and counter anions are explored instead of high sodium chloride concentrations to produce more beneficial “mobile nutrient” solutions. Possible alternatives to NaCl include NaOH and  $\text{KNO}_3$ . The alternative salts are identified based on the similar IX capacities of basic salts ( $\text{OH}^-$ ) and nitrates ( $\text{NO}_3^-$ ) to chlorides ( $\text{Cl}^-$ ) (Clifford et al., 2011). Moreover, potassium could be an alternative cation for the eluent (George et al., 2012) because it is another essential micronutrient for plants and a critical ingredient for apatite formation (Basak et al., 2018; Wilsenach et al., 2007) if a subsequent precipitation step were desired.

Thus, the systematic effects of pH, SOM and HLR on ortho-P recovery using IX from actual ADs supernatant were firstly studied towards creating a mobile nutrients solution containing suitable N/P/K mass ratio to balance deficient fertilizer and facilitate agricultural reuse. Accordingly, the objective of this paper was to

examine the water chemistry and operational conditions during loading and regenerating. Packed bed column experiments were conducted using a commercially available SBAX resin to capture ortho-P ions over a range of pH conditions and explored the absence versus presence of SOM from ADs. Breakthrough curves for ortho-P under different HLR were evaluated to minimize the length of the mass transfer zone (i.e., sharp breakthrough). Both the flow rates and composition of the regeneration solutions were varied to maximize the concentration of ortho-P in the regenerant solution and minimize the sodium concentration. The replacement of chloride ions with hydroxide or nitrate ions was also explored as a means to improve the quality of the recovered, concentrated, mobile ortho-P nutrient solution.

## 2. Materials and methods

A type-1 strong-base anion exchange (SBAX) resin with water content of 50%–60% and quaternary amine exchange functional groups in chloride ion form (21K-XLT, Dowex) was used. It has a general ion-exchange (IX) capacity of 1.4 equivalents/L. The physical state of the SBAX resin was yellow spherical beads with particles 0.3–1.2 mm in diameter and uniformity coefficient  $\leq 1.1$  (Kalaruban et al., 2016; Ok and Jeon, 2014). The approach outlined was similar for other IX resins, but the capacities and selectivity differ. All other chemicals were analytical grade, purchased from Merck, and were used as received without further purification.

### 2.1. Model water and anaerobic digested water

Model orthophosphate (ortho-P) water was prepared by dissolving ortho-P in ultrapure water (Millipore Inc.). Ortho-P solutions of 500 mg P/L were prepared using monobasic sodium phosphate ( $\text{NaH}_2\text{PO}_4$ ) or dibasic sodium phosphate ( $\text{Na}_2\text{HPO}_4$ ) with different solution pH of 4.5 and 9.0, respectively, without further pH adjustment.

Anaerobic digester supernatant was collected from a full-scale denitrifying activated sludge WWTP in the metro-Phoenix area (Arizona, USA). Before used, the supernatant was filtered with a 1.2  $\mu\text{m}$  inline filter system. The ortho-P concentration of the raw supernatant was  $\sim 200$  mg P/L and was increased to 500 mg P/L by adding  $\text{KH}_2\text{PO}_4$ . This served as the feed wastewater for IX and was the same concentration as the model water.

### 2.2. Ion exchange experimental apparatus and operation

Packed bed IX column tests were performed using 75 g of SBAX resin in a glass column (inner diameter, 2.5 cm), giving a bed depth of 23.0 cm with an empty bed volume (BV) of 113  $\text{cm}^3$ . The resin was supported by glass beads to ensure even flow distribution. The resin was packed as a slurry into a column containing water and rinsed with deionized water to minimize air entrainment. Ortho-P solutions (500 mg P/L) were pumped upward through the column using a controllable flow peristaltic pump. Hydraulic loading rate (HLR) effects were investigated by adjusting flow rates between 3 and 10 BV/h (with HLR of 0.69–2.30 m/h). The influent solution was varied for different tests. To develop breakthrough curves, effluent samples were collected periodically and analysed for ortho-P. The packed bed was operated until a complete ortho-P breakthrough was obtained. The total mass of ortho-P loaded on the resin was calculated by summing the differences between the influent and effluent concentrations for each sample and multiplying by the volume treated in the time segment (area above the curve). After breakthrough, the IX column loaded with ortho-P was regenerated in a down-flow mode using salt brines with a low flow rate of 2 or 3 BV/h.

Separate batch desorption tests were conducted using different brine compositions (NaCl, NaOH, and KNO<sub>3</sub>) and salt concentrations. In this experiment, the ortho-P loaded resin was dispersed in a 100 mL eluent solution and stirred for 12 h. Desorption efficiencies were calculated as a ratio of the desorbed ortho-P amount to the initially loaded ortho-P amount.

### 2.3. Analytical methods

Phosphate concentrations (in mg P/L), not including the organic phosphate fraction which always accounts for approximately 5%–10% of the total phosphate (Xu et al., 2015), were analysed using ion chromatography (Dionex DX-120; AS12A column). Water quality parameters, such as chemical oxygen demand (COD), dissolved organic carbon (DOC), and ultraviolet–visible (UV) absorption at 254 nm (UV<sub>254</sub>), were measured following standard methods (American Public Health et al., 1915). The pH, UV<sub>254</sub>, COD, and DOC values were individually detected using a pH meter (PHS-3C), a ultraviolet–visible spectrophotometer (UV-1800, Shimadzu, Japan), closed reflux dichromate colorimetric method 5220 D, and total organic carbon analyser (Shimadzu TOC-V CSH), respectively. UV<sub>254</sub> is an index that represents aromatic materials and materials with conjugated double bonds (Ates et al., 2007).

## 3. Results and discussion

### 3.1. Efficiency of ortho-P capture with different influent ortho-P species

Fig. 1a shows breakthrough curves for ortho-P solutions at pH 4.5 and 9.0. The speciation of the ortho-P species is also shown in Fig. 1a, indicating that the di- or mono-hydrogen phosphate influent species dominate at pH 4.5 and 9.0, respectively (Li et al., 2017; Zhou et al., 2012). These experiments were performed with HLR (0.69 m/h), which is considered very low (HLR ~ 25 m/h) for treating ortho-P to achieve target effluent levels (Ngo Thuy Diem et al., 2010; Yang et al., 2017). The low HLR resulted in a period of near complete ortho-P removal, followed by sharp breakthroughs between 40 BV at pH 9.0 and 80 BV at pH 4.5. In these experiments, between 90% and 92% of the influent ortho-P was captured by the IX resin before the experiment was stopped. The total capacities of the IX resin with influent pH levels of 4.5 or 9.0 were 64.2 and 36.7 mg P/g, respectively.

On a charge-equivalence basis the exchange capacity of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (pH 4.5) should be twice that of HPO<sub>4</sub><sup>2-</sup> (pH 9.0). However, the actual ratio was only 1.75. This is possibly because the feed pH influences retention and selectivity by affecting the functional group form of the resin and forms of the solute ions (Federation and American Public Health, 2005). First, as ortho-P ions exchanged with chloride on the surface of the IX resin, the solution pH and buffering capacity changed. By removing >90% of the ortho-P, the low H<sub>2</sub>PO<sub>4</sub><sup>-</sup> concentration (<50 mg P/L) in solution made the pH increase to about 6.0, while the low HPO<sub>4</sub><sup>2-</sup> concentration (<50 mg P/L) made the pH decrease to less than 7.0. In these cases, an interconversion between the two ortho-P species occurred, affecting the IX capacity. Second, while HPO<sub>4</sub><sup>2-</sup> contains 2 eq/mole versus 1 eq/mole for H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, the polymeric backbone of the SBAX resin may preclude the close proximity of two H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ions directly adjacent to one another (An et al., 2013; Maul et al., 2014). However, anions with a higher charge would interact more strongly with the resin (Wilsenach et al., 2007); therefore, SBAX resin has better selectivity for HPO<sub>4</sub><sup>2-</sup> than H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. These findings are consistent with the literature where pH affects the selectivity of IX resins for ortho-P species at different pH levels (Ding et al., 2012; Sowmya and Meenakshi, 2013). Careful selection of the counter anion

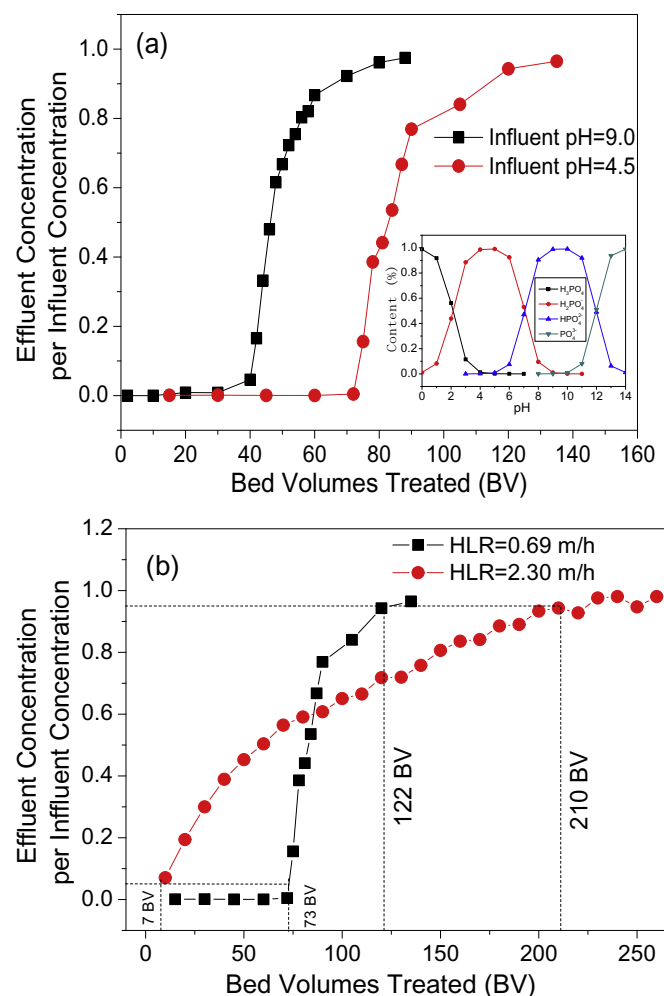


Fig. 1. Optimized operating conditions for enhancing ortho-P uptake in columnar experiments. (a) Ortho-P uptake at different pH with an initial ortho-P concentration of 500 mg P/L and HLR of 0.69 m/h. (b) Ortho-P uptake at different HLRs with an initial ortho-P concentration of 500 mg P/L and influent pH of 4.5.

(chloride, sulphate) in the acid should be considered, as to not result in greater competition between the counter anion and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ion.

### 3.2. Efficiency of ortho-P capture with different HLR

Fig. 1b shows that increasing HLR resulted in a less sharp breakthrough curve, indicating a longer mass transfer zone. To maximize ortho-P capture, a shorter mass transfer that results in near complete ortho-P capture is desired to minimize the volume of elute and maximize the ortho-P concentration in the recovered solution (i.e., HLR = 0.69 m/h). The initial ortho-P breakthrough was only 7 BV of treated water at HLR = 2.30 m/h, compared with 73 BV at HLR = 0.69 m/h. Experiments were stopped when nearly complete ortho-P breakthrough occurred (122 or 210 BV). At the end of the experiments, the capacity of the IX resins was calculated to be nearly equivalent (35.6 versus 31.5 mg P/g resin at 0.69 and 2.30 m/h, respectively). Thus, from an ortho-P removal perspective, both HLR were nearly equivalent. To maximize capture of ortho-P using IX, these results suggest using a low HLR (i.e., 0.69 m/h) and treatment of a finite number of BVs (i.e., ~73 BV) before regeneration and recovery of captured ortho-P. In the future, an on-line ortho-P sensor could be used to optimize the time for

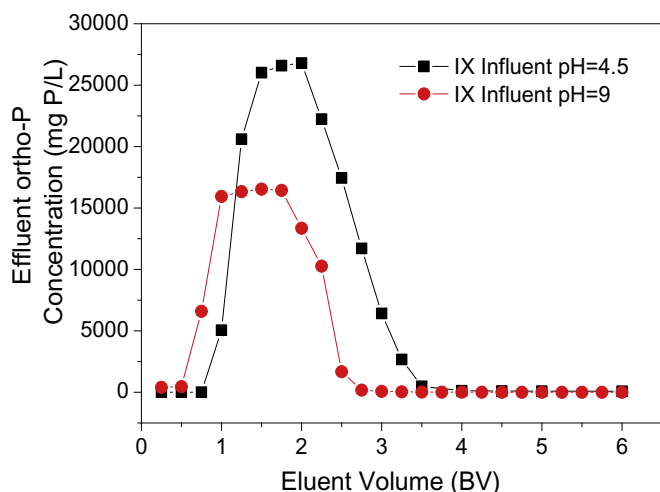


Fig. 2. Desorption of different ortho-P species with 1 N NaCl at a flow rate of 2 BV/h in columnar experiments.

breakthrough and regeneration.

The observed breakthrough behaviour was consistent with findings by others and can be explained on the basis of mass transfer fundamentals (Zeng et al., 2008). The mass transfer zone is a complex function of the ratio of mass transfer rates (film to intra-resin particle diffusion rates), which varies with flow rate, axial dispersion, resin diameter, exchange/sorption kinetics, and liquid phase ion diffusivity coefficients. When other factors are held constant, the length of the mass transfer zone increases with higher HLR. A shorter mass transfer zone is desired to maximize ortho-P capture.

### 3.3. Ortho-P recovery from saturated IX resins

Fig. 2 shows an elution profile using 1 N NaCl on IX resins saturated with ortho-P at pH 4.5 or 9.0. (Breakthrough curves of the same columns are illustrated in Fig. 1.) Samples were collected and analysed separately at each point on the regeneration curve. The two curves in Fig. 2 exhibited similar trends. The regenerant ortho-P concentrations increased over the first 2 BV, and then declined, with near complete elution of ortho-P by 4–5 BV of the 1 N NaCl solution. The maximum effluent ortho-P concentration with IX loaded at pH<sub>0</sub> 4.5 was 27,500 mg P/L, which was much higher than 17,000 mg P/L from IX loaded at pH<sub>0</sub> 9.0. Almost 95% of the exchanged ortho-P was eluted within 3.5 BV from IX loaded at pH<sub>0</sub> 4.5 and 3.0 BV from IX loaded at pH<sub>0</sub> 9.0. The ortho-P desorption, recovery efficiencies and recovered ortho-P concentrations are presented in Table 1. The ortho-P recovery efficiency was similar between the two columns (79% or 81%), but the recovered ortho-P concentration was substantially higher (17.8 mg P/L) for the IX resin loaded at pH 4.5 compared to the IX column loaded at pH 9.0 (only 8.9 mg P/L).

### 3.4. Comparison of regenerant brine cation and anion composition

Changing the composition of the regenerant brine is feasible and may make it more suitable to create mobile nutrients that are compatible with subsequent agricultural fertilizer use (Johnston and Richards, 2003; Sengupta and Pandit, 2011). Fig. 3a compares ortho-P desorption with different eluents in batch tests. A 1 N NaCl solution achieved the best desorption efficiency of 88%. Recovery efficiencies using 1 N NaOH were 64%, which was slight better than 60% recovery efficiencies using 1 N KNO<sub>3</sub>.

In a packed bed configuration, it should be possible to modify the brine concentrations or adjust the number of BV treated by brine to achieve a similar performance among the brines of NaCl, NaOH and KNO<sub>3</sub>. Additional tests compared NaOH brine regenerant concentrations (0.05, 0.1, 0.5, and 1 N). Fig. 3b shows that the desorption efficiency declined at lower NaOH concentrations. This relates to the number of exchangeable equivalents of charge (OH<sup>−</sup> versus phosphate ions) and concentration gradients rather than the selectivity of OH<sup>−</sup> against ortho-P ions.

Because OH<sup>−</sup> exhibited a slightly better regeneration performance than NO<sub>3</sub><sup>−</sup>, and K is an essential element of plant growth. Moreover, there is no difference to change metal cation such as K salt or Na salt. Thus, the use of KOH to regenerate a saturated column was evaluated. Fig. 4 shows the results from an IX column loaded with ortho-P at a pH<sub>0</sub> of 4.5. Fig. 4a shows a slightly broader desorption peak for 0.5 N KOH than that observed with 1 N NaCl (Fig. 2), which would be expected based upon the concentration of exchangeable ions. The maximum ortho-P concentration reached 12,000 mg P/L. The IX resin was nearly completely regenerated within 6 BVs. This is approximately twice as many BV compared to the more concentrated 1 N NaCl regeneration experiment (Fig. 2), which is equivalent on a charge basis. All subsequent regenerations used 0.5 N KOH regeneration brine.

In addition to measuring ortho-P elution (Fig. 4a), we simultaneously monitored the pH in the regeneration solution (Fig. 4b). The pH of the influent 0.5 N KOH solution was 13.3. Passage of 0.5–3.5 BV of the regenerant solution increased the effluent pH from 5.0 to 7.0. A sharp increase in the pH was observed after 3.7 BV (Fig. 4b), and this corresponds with a decline in the elution ortho-P concentration (Fig. 4a). This pH jump occurs as the number of exchangeable sites on the resin becomes saturated with OH<sup>−</sup>. Additionally, the buffering capacity of the ortho-P in solution declines as less ortho-P is desorbed from the resin. Thus, pH could be measured as an operational tool to track (and optimize) the desorption/regeneration cycling of the IX resin. Furthermore, monitoring the effluent pH could be used to target the desired pH of the mobile nutrient solution, thereby optimizing it for soil addition.

### 3.5. Effect of organic matter on capturing ortho-P

The influence of organic acids on ortho-P uptake was investigated using supernatant fermentation liquor spiked with an ortho-P concentration similar to that used in the model waters

Table 1  
Ortho-P uptake and ortho-P recovery at various pH<sub>0</sub> and in presence of soluble organic matter (SOM).

Parameter	Model Water	Model Water	Model Water	ADs supernatant containing SOM
IX Column Influent pH	4.5	9.0	7.5	7.5
IX Capacity (mg P/g resin)	64.2	36.7	52*	14.3
Ortho-P capture efficiency	92%	90%	—	48%
Ortho-P desorption efficiency	88%	87%	—	88%
Net ortho-P recovery efficiency	81%	79%	—	43%
Mobile Nutrient - Recovered ortho-P solution concentration (g P/L)	17.8	8.9	—	2.0

\*IX capacity in model water at pH 7.5 was estimated based upon other model water experiments and ortho-P speciation.



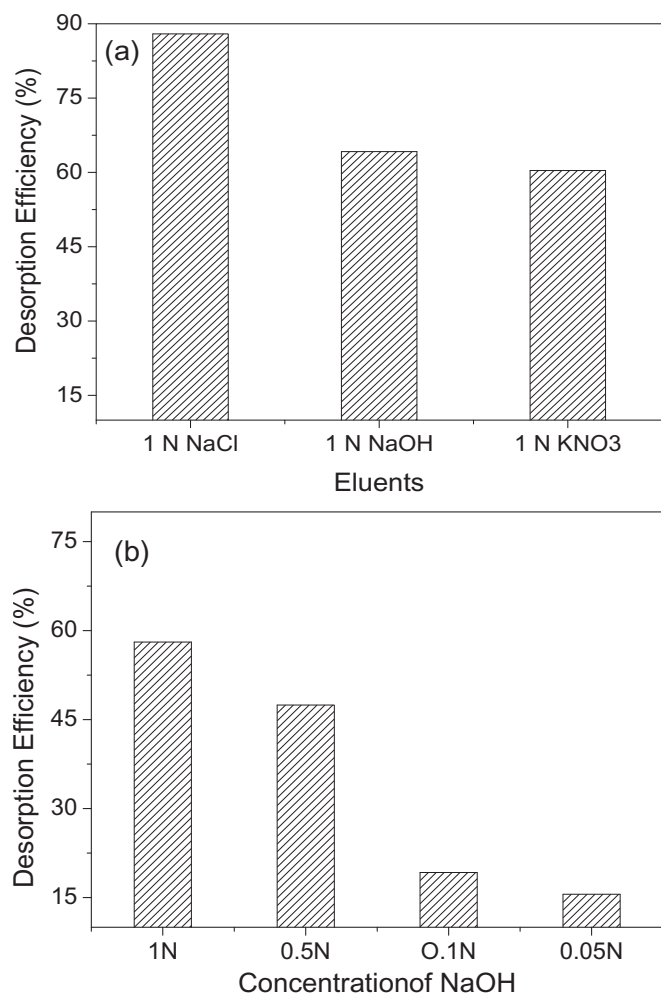


Fig. 3. Batch tests of ortho-P desorption by (a) different eluents and (b) NaOH at different concentrations.

investigated above. Fig. 5a shows the breakthrough profiles for ortho-P, COD, and DOC; influent concentrations were 500 mg P/L, 556 mg/L, and 100 mg/L, respectively. The influent pH was 7.5. The HLR was 0.69 m/h. Compared to Fig. 1, the breakthrough of ortho-P was more gradual, with a longer mass transfer zone. Simultaneously, large amounts of COD and DOC were removed. Therefore, the shape of the mass transfer zone for ortho-P is influenced by competition for the sorption sites (Obaja et al., 2003). Achieving higher COD removal in the anaerobic digester could, presumably, reduce this competition.

Upon complete breakthrough of ortho-P at roughly 47 BV, the exchange capacity of the IX resin was calculated to be 14.3 mg P/g resin. Based upon the speciation of ortho-P and previous results, the exchange capacity of 500 mg P/L at pH 7.5 in ultrapure water was estimated to be 52 mg P/g (Table 1). As listed in Table 2, phosphate adsorption capacity of those reported materials in wastewater (urine and ADs supernatant) was similar with that of SBAX resin in this study, except calcined ZnAl-LDH in sludge filtrate with low phosphate concentration. Moreover, phosphate adsorption capacity of reported materials was a slight decrease in seawater or lake water which may be attributed to the low SOM. The presence of SOM in the digester effluent and other potential anions (i.e., bicarbonate with a concentration of about 3000–4000 mg/L or higher as CaCO<sub>3</sub> in digester effluents) (Gifford et al., 2015)) reduced the ortho-P capacity by 48%. This finding is

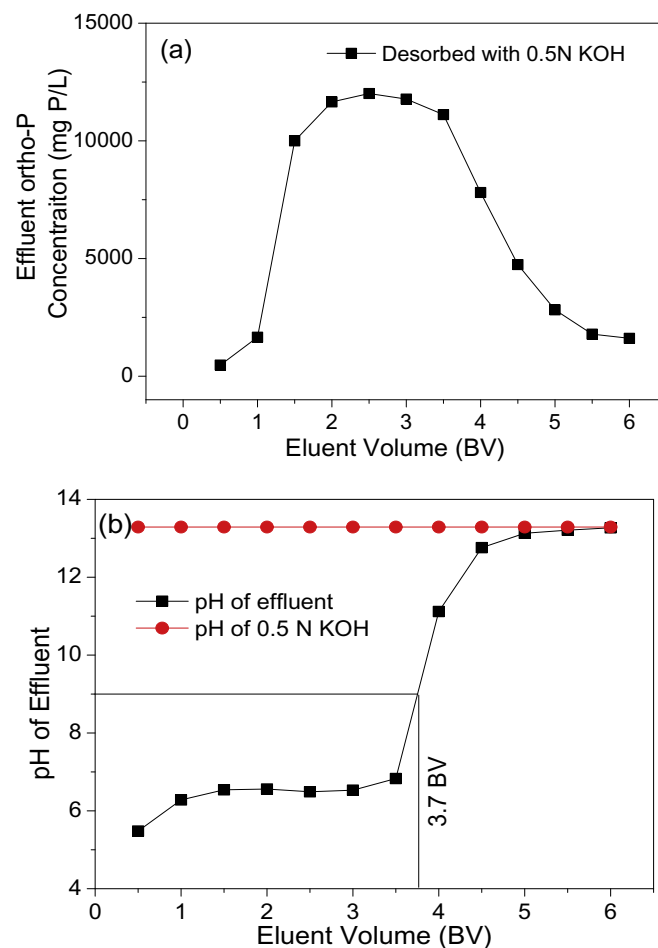


Fig. 4. Column tests of ortho-P desorption with 0.5 N KOH at a flow rate of 2 BV/h (The IX resin was loaded at pH 4.5.) (a). The effluent pH value (b).

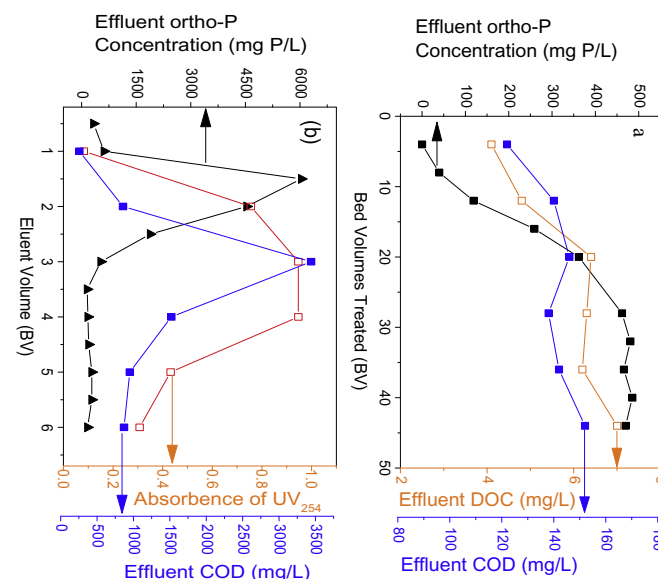


Fig. 5. Performance of IX of ortho-P from wastewater in columnar tests. (a) Ion exchange of ortho-P, COD, and DOC at a flow rate of 0.69 m/h. (b) Desorption of ortho-P by 0.5 N KOH at a flow rate of 2 BV/h.

**Table 2**

Comparison of phosphate recovery with various materials in different water category.

Materials	Water category	Dosage (g); Initial phosphate concentration (mg P/L)	Adsorption capacity (mg P/g) in model water	Adsorption efficiency (%) or capacity (mg P/g) in practical application	Desorption efficiency (regeneration reagent)	References
Bay oxide loaded Mn or Ag	Lake water	0.1–1.5; 5	25.5–38.9	94.0–99.9%	60–80% (0.1 M NaOH)	Lalley et al. (2016)
Resin loaded lanthanum	Seawater	2.0; 155	9.60	7.40	95% (6 M HCl)	Wu et al. (2007)
Calcined ZnAl-LDH	Sludge filtrate	0.02–0.1; 20	—	35.8	80% (5% NaOH)	Cheng et al. (2009)
Resin loaded hydrous ferric oxide	Urine	~30; 668	—	10.0	92% (2.5% NaCl/2.0% NaOH)	O'Neal and Boyer (2013)
Resin loaded hydrous ferric oxide	ADs supernatant	~15; 82.5	—	12.1–13.4	92% (2.5% NaCl/2.0% NaOH)	O'Neal and Boyer (2013)
SBAX resin	ADs supernatant	75; 500	36.7–64.2	14.3	87–88% (0.5 N NaOH)	This study

consistent with previous work noting that the competition between ortho-P and organic matter for anion exchange sites reduced the sorption capacity from model water to wastewater by about half (Geelhoed et al., 1998; Gifford et al., 2015). Thus, the obvious decreased phosphate adsorption using wastewater is believed to be caused by the presence of SOM. An IX resin more selective toward ortho-P ions could reduce the impact of the competing ions on the reduced ortho-P exchange capacity in complex water matrices.

Fig. 5b shows the desorption profile for a saturated SBAX resin with 0.5 N KOH for elution. The ortho-P desorption recovery efficiencies and recovered ortho-P concentration in the presence of SOM were calculated in Table 1. Fig. 5b shows that complete ortho-P recovery was attained within 3.5 BV, with a maximum ortho-P concentration being achieved at 1.75 BV. The efficiency of ortho-P desorption was high (88%) and comparable with the model water experiments (Table 1). Compared with desorption efficiency of other materials, SBAX resin had better desorption efficiency with low concentration of regeneration reagent (Table 2). The net efficiency of ortho-P capture and recovery was 43%, lower than the model waters. The recovered ortho-P solution had a concentration of 2.0 g P/L. The maximum eluted ortho-P concentration occurred earlier than that of COD or UV<sub>254</sub> and offered the opportunity to selectively capture ortho-P with a low COD content in the eluted and captured ortho-P solution. It may be possible to use UV<sub>254</sub> measurements as a real-time indicator for this separation, if a low COD concentration is desired in the mobile nutrient solution.

Switching from sodium to potassium cations in the brine was shown to be feasible. This demonstration is important because sodium inhibits plant growth, whereas potassium is an essential plant nutrient. Switching from chloride to hydroxide anions is also feasible. The benefits of a higher pH, concentrated ortho-P recovered solution are numerous, including avoidance of chloride contamination of groundwater or potential formation of solid-phase fertilizers. While we did not explicitly investigate ammonium ion recovery using cation exchange processes, this approach is possible. And effluents from the anion and cation exchange resins could be combined (along with magnesium addition) to produce struvite as a mobile nutrient. However, agricultural research shows that struvite may not be an ideal rapid release fertilizer (Hao et al., 2013; Rittmann et al., 2011). It may also be possible, although this approach is not investigated in this study, to elute ortho-P from the IX resin using a blend of potassium and ammonium nitrate brine. Because OH<sup>−</sup> exhibited similar regeneration performance with NO<sub>3</sub><sup>−</sup>, and K is an essential element of plant growth, the use of 0.5 N KNO<sub>3</sub> to desorb a saturated column in ADs supernatant was evaluated. The effluent ortho-P solution contained essential element (N, ortho-P and K) for fertilizer. The mass ratio of N/ortho-P/K was calculated as 17:8:75 based on recovered ortho-P concentration

from ADs in Tables 1 and 0.5 N KNO<sub>3</sub>. This N/ortho-P ratio is consistent with the estimated ratio of overall efficiency of applied fertilizer (Baligar et al., 2007), but the K ratio is slightly excessive, which is because K was not an exchanged ion. Therefore, this desorption solution could be used to balance deficient fertilizer, without the application of excessive amounts of a single nutrient (Jakobsen, 1993a, b).

#### 4. Conclusions

This paper presented a study concerning the recovery of phosphate from ADs supernatant with a high concentration of phosphate (500 mg P/L) by IX technology. The IX capacity increased by shifting the speciation from HPO<sub>4</sub><sup>2−</sup> towards H<sub>2</sub>PO<sub>4</sub><sup>−</sup>, with the IX capacities of 64.2 mg P/g and 36.7 mg P/g, respectively. The HLR of 0.69 m/h (3 BV/h) was desired to capture ortho-P, with about 90% ortho-P capture efficiency and about 80% recovery efficiency, respectively. Switching from NaCl to NaOH and KNO<sub>3</sub> brines as eluents to desorb ortho-P was feasible to reduce the harmful effect on soil or plants in applications. The ortho-P capture capacity with ADs supernatant was 14.3 mg P/g, with great disturbance of SOM. Over 85% ortho-P recovery efficiency was attained in the presence of both ortho-P and SOM. The resulting solution after eluting ortho-P using KNO<sub>3</sub> contains a desired N/ortho-P/K mass ratio (17:8:75) to balance deficient fertilizer. This study advances understanding of recovery of phosphate from wastewater streams used as “mobile nutrient” for agriculture.

#### Acknowledgements

This study was financially supported by the US National Science Foundation (BCS-1026865 and EEC-1449500), the US Environmental Protection Agency (RD83558001), the National Natural Science Foundation of China (51778352, 51578329), the Science and Technology Commission of Shanghai Municipality (16010500200, 18230710900), and the Program for Innovative Research Team in University (IRT13078). Thanks are due to Yu Yang at Arizona State University, who provided considerable assistance on the lab work.

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