

Mechanisms of phosphorus removal from wastewater by ion exchange resin

Chaowei Zhu^{a,b}, Qiaoying Wang^{a,*}, Weihai Pang^a, Zhiwei Wang^a, Jing Cao^c, Weijie Hu^c,
Jianguo Tang^d, Jin Huang^d, Zhichao Wu^a

^aState Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China, email: zhucw@craes.org.cn (C. Zhu), Tel. +86 21 65980400, email: qywang@tongji.edu.cn (Q. Wang), pangweihai@tongji.edu.cn (W. Pang), zwwang@tongji.edu.cn (Z. Wang), wuzhichao@tongji.edu.cn (Z. Wu)

^bChinese Research Academy of Environmental Sciences, Beijing 100012, China,

^cShanghai Municipal Engineering Design Institute (Group) Co., LTD, 901 North Zhongshan Road (2nd), Shanghai 200092, China, email: 174586596@qq.com (J. Cao), 1097377639@qq.com (W. Hu)

^dShanghai Urban Construction Design & Research Institute (Group) Co., LTD, 3447 Dongfang Road, Shanghai 200125, China, 278168298@qq.com (J. Tang), 83915057@qq.com (J. Huang)

Received 7 August 2016; Accepted 11 May 2017

ABSTRACT

This study investigated the mechanisms of phosphorus removal from both synthetic wastewater and effluent of an anaerobic membrane bioreactor (AnMBR) treating sewage by ion exchange resin. The results showed that 88.6% of phosphorous could be removed from the effluent of AnMBR with dosage of 10.0 g/L Amberlite IRA-958 resin, suggesting that ion exchange is a promising method for removing phosphorus from real wastewater. The maximal equilibrium sorption capacity of phosphate (Q_e) was obtained at pH 10 for both synthetic wastewater and real wastewater. However, the isothermal sorption model and sorption kinetics of phosphate from synthetic wastewater were different from those of real wastewater due to the complexity of real wastewater. The phosphate sorption capacity and sorption equilibrium time of Amberlite IRA-958 resin in real wastewater were lower than that in synthetic wastewater. Furthermore, the sorption behaviors of synthetic wastewater fitted well with Langmuir isothermal sorption, while those of real wastewater were in agreement with Freundlich isothermal sorption. The results also show that the kinetics of phosphate sorption onto Amberlite IRA-958 resin from both real wastewater and synthetic wastewater corresponded well with the pseudo-first order kinetics model. The regeneration experimental results show that 0.4 mol/L NaCl could be used as the effective regeneration solution to recover the resin.

Keywords: Phosphorus removal; Ion exchange; Isothermal sorption models; Anaerobic membrane bioreactor; Wastewater treatment

1. Introduction

Phosphorus (P) is well known as a nutrient that induces eutrophication of aqueous ecosystems, and is considered to be one of the key pollutants released from wastewater treatment plants (WWTPs). Studies [1,2] have reported that eutrophication is accelerated when the concentration of phosphorus in lake water exceeds 0.02 mg/L. However, the influent concentration of total phosphorus in WWTPs

is generally in the range of 4–9 mg/L [3,4], which is much higher than the natural assimilation capacity of rivers and lakes. Therefore, removing phosphorus from wastewaters is of great urgency for protecting the aquatic environment.

On the other hand, phosphorus is an important resource used in agriculture and many other industries [5,6], while phosphate ore, the world's dominant source of phosphorus, is very limited. It has been reported that with current world reserves, phosphate ores will last an estimated 30–300 years [7,8]. Globally, about 1.3×10^9 kg phosphorus per year is treated in WWTPs, which could be considered as the

*Corresponding author.

major alternative source of phosphorus [9]. Yuan et al. [10] reported that approximately 15–20% of total phosphorus demand could be satisfied by recovering the phosphorus from real domestic sewage. Previous reports have verified the feasibility of producing ammonium magnesium phosphate from recovered phosphorus as a valuable agricultural fertilizer [11,12]. Thus, considering the resource-depleting effects of phosphorus, establishing how to efficiently and economically recover phosphorus from effluent of WWTPs is a pressing matter.

Several biological, physical and chemical processes have been widely studied to remove pollutants in water and wastewaters. Compared with chemical technologies, phosphate removal via biological methods is more economical and environmentally friendly. The activated sludge (AS) system has been used as the preferred biological technology to remove phosphorus from municipal wastewater for the last 40 years. Currently, biological processes, such as anaerobic/anoxic/oxic (A/A/O), oxidation ditch, sequencing batch reactor (SBR), and membrane bioreactor (MBR) have been extensively employed for domestic wastewaters treatment in WWTPs [4]. Among these, an anaerobic membrane bioreactor (AnMBR) has successfully established itself as a robust treatment technology for domestic wastewater, which thanks to their advantages of low energy consumption, high load, and recyclable energy [13,14]. However, under anaerobic conditions, ammonification and phosphorus released by microorganisms results in increased nutrient concentrations in the effluent of AnMBRs [15]. To obtain higher phosphorus removal efficiencies, an advanced treatment process or physicochemical approach needs to be combined with the AnMBR process [16,17].

Among all the physicochemical approaches, the ion exchange method has been identified as a feasible alternative due to its operational simplicity and adaptability to various wastewater characteristics [18,19]. It has been reported that some polymeric anion exchange resins have specific selectivity for phosphate, and the process is reversible [20,21]. The adsorbed phosphate can be collected and recycled by backwashing, and the ion exchange resin can be regenerated [22,23]. The high selective capacity of ion exchange method is one of their major superiority over other techniques, which could obtain the recovered products with high purity to avoid the toxicity of contaminants. Thus, the ion exchange method is considered to be an environmentally friendly method, and benefits the sustainable management of phosphorus resources [24]. Efforts are made to study the phosphorus removal mechanisms by ion exchange method and test the feasibility of practical application of ion exchange method in WWTPs. Nowadays, a variety of sorbents have been reported for selectively removing nitrate, such as macro-reticulated Amberlite IRA-900 [25], Dowex SBRP [26], Purolite A520E [27], Purolite A100 [28], and Purolite A300 [29]. However, investigation into an ion exchange resin for phosphorus removal from wastewater are relatively limited [11,30].

In this study, an anion exchange resin, Amberlite IRA-958, was adopted to remove phosphorus from both AnMBR effluent and synthetic wastewater. The influences of dosage, contact time, pH, and competing anions on the removal efficiency of phosphorus were investigated. Sorption kinetics

models, isotherms sorption models, and the rate-limiting steps of phosphorus on the ion exchange resin were also determined. Finally, the optimal concentration of regeneration solution for the resin was selected. The results obtained in this study are expected to provide a sound understanding of the removal of phosphorus using the ion exchange method.

2. Materials and methods

2.1. Materials and analysis methods

The strong-base ion exchange resin named Amberlite IRA-958 (Rohm and Haas, United States) was used in this study, and its properties are shown in Table 1. The resin was activated before all the experiments using the Chinese standard method (GB/T 5476–1996). The resin was firstly washed with deionized (DI) water until there were no impurities in the eluent. The resin was then put into an ion exchange column and flushed with the following in the stated order: 1 M NaOH, DI water, 1 M HCl, and DI water, with each solution made up to 400 mL. The flushing procedure was repeated until the final elution was yellow when methyl orange was added.

To analyze the sorption kinetics of phosphate by ion exchange resin, AnMBR effluent (real wastewater) and synthetic wastewater with the same concentration of phosphate were prepared. AnMBR effluent was obtained from a pilot-scale anaerobic MBR setup, and filtered using a 50 μm mesh strainer to remove large particles. The $\text{PO}_4^{3-}\text{-P}$ concentration in the AnMBR effluent was adjusted to 9.0 mg/L with Na_2HPO_4 before all the experiments. Na_2HPO_4 was used to prepare synthetic wastewater and maintain the same $\text{PO}_4^{3-}\text{-P}$ concentration (9.0 mg/L) as that of AnMBR effluent.

Measurements of $\text{PO}_4^{3-}\text{-P}$, total nitrogen (TN), ammonia ($\text{NH}_4^+\text{-N}$), nitrite ($\text{NO}_2^-\text{-N}$), and nitrate ($\text{NO}_3^-\text{-N}$) in the AnMBR effluent were performed according to Standard Methods [31]. The total organic carbon (TOC) concentration of the AnMBR effluent was determined in order to represent the soluble organic constituents (TOC-VCPN, Shimadzu, Japan). The concentration ranges of TOC, TN, $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, $\text{NO}_2^-\text{-N}$, and total phosphorus (TP) were 6.0–10.1, 27.4–52.4, 20.7–44.6, 0.1–1.4, 0–4.5, and 8.2–10.4 mg/L, respectively. Detailed information is provided in our previous study [32].

Table 1
Physicochemical properties of the Amberlite IRA-958 resin

	Amberlite IRA-958
Appearance	White, opaque
Product type	Macroporous, strong-base
Ionic form	Cl^-
Functional group	$-\text{N}^+(\text{CH}_3)_3$
Size (mm)	0.63–0.85
Moisture (%)	66–72

2.2. Batch experiments

2.2.1. Effects of resin dosage on phosphate removal

To investigate the effects of resin dosage on phosphate removal in AnMBR effluent, different dosages of Amberlite IRA-958 were added to conical flasks with 100 mL AnMBR effluent to form suspensions with 1.0, 2.0, 4.0, 6.0, 8.0, and 10 g/L Amberlite IRA-958, respectively. Since the phosphate sorption capacity of resin in synthetic wastewater was expected to be higher than that in real wastewater, the concentrations of Amberlite IRA-958 in synthetic wastewater were set as 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 g/L to remove phosphate in synthetic wastewater. All samples were collected after oscillation in a vibrator at 298 K and 120 rpm for 24 h at pH 10, which was measured using a pH meter (Starter 3100, OHAUS, America).

The phosphate sorption capacity of resin in real wastewater and synthetic wastewater was calculated according to the following equations:

$$Q_e = V \frac{(C_0 - C_e)}{m} \quad (1)$$

$$Q_{e, \text{ dry resin}} = \frac{Q_{e, \text{ wet resin}}}{(1 - \eta)} \quad (2)$$

where Q_e is the equilibrium sorption capacity of the resin (mg/g); V is the solution volume (L); C_0 and C_e are the initial and equilibrium phosphate concentrations in the solution (mg/L), respectively; m is the mass of resin (g); and η is the moisture (%), which was detected according to the Chinese standard method (GB/T 5757–2008).

2.2.2. Effects of pH and competing anions on phosphate removal

To investigate the effects of pH and anions on phosphate removal by ion exchange resin, three different types of synthetic wastewater contained 290 mM of Cl^- , NO_3^- , and SO_4^{2-} was prepared with NaCl, NaNO_3 , and Na_2SO_4 , respectively, which was the equivalent molar concentration of PO_4^{3-} . The concentration of anions was measured with a total dissolved solid meter (SC-2300, SUNTEX, China). The synthetic wastewater was divided into five conical flasks. Each contained 100 mL of solution, and the pH of the solutions was adjusted with NaOH and HCl to measure 4, 6, 8, 10 and 12 respectively. All the conical flasks were set in a vibrator to oscillate at 120 rpm and 298 K with a dose of 1.0 g/L resin. The phosphate concentration was determined after 24 h, and the equilibrium sorption capacity of phosphate was calculated according to Eqs. (1) and (2).

2.2.3. Effects of contact time on phosphate removal

A fixed amount of AnMBR effluent and synthetic wastewater with same phosphate concentrations was added to two respective beakers, then 1.0 g/L resin was added to each. The beakers were oscillated in a vibrator at 120 rpm and 298 K. The phosphate concentration was determined after specific time intervals, and the equilibrium sorption capacity of phosphate was calculated using Eqs. (1) and (2).

2.2.4. Regeneration experiments

AnMBR effluent (100 mL) was injected to five conical flasks, respectively, and Amberlite IRA-958 with a dose of 10 g/L was added in to each flask. The flasks were put in a vibrator at 298 K and 120 rpm for 24 h, and Q_e was calculated after the sorption procedure. The five identical exhausted resin was then washed with deionized water, and regenerated with 25 mL of regeneration solution containing 0.2, 0.4, 0.6, 0.8 and 1.0 mol/L NaCl for 15 min, respectively. The regenerated resins were then washed with deionized water to conduct the same sorption procedure, and the sorption capacity of the regenerated resin was calculated to obtain the recovery rate of Q_e . The sorption and regeneration procedure of the same resin was repeated three times to obtain the variation of the recovery rate of Q_e of each cycle. The whole regeneration experiments were repeated twice to get the reduplicative data.

3. Results and discussion

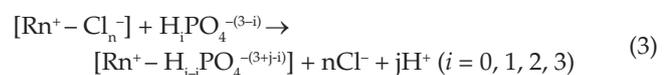
3.1. Effects of resin dosage on phosphorus removal

The removal rate and phosphate Q_e of Amberlite IRA-958 from both AnMBR effluent and synthetic wastewater are shown in Fig. 1. The removal rate of phosphate increased with increasing resin dosage, and Q_e decreased with increasing resin dosage for both AnMBR effluent and synthetic wastewater. However, the sorption capacity in synthetic wastewater was much higher than that in AnMBR effluent. In synthetic wastewater, the sorption capacity was 24.6 mg/g (resin), and the removal rate by 1.0 g/L Amberlite IRA-958 reached 88.6%. In AnMBR effluent, these figures were 10.0 mg/g (resin) and 33.6%, respectively, with the same amount of resin. To achieve the same removal rate in the case of AnMBR effluent as with the synthetic solution (88.6%), a resin dose of 10 g/L had to be used to treat AnMBR effluent. This result indicates that the complex composition of real wastewater, and the existence of inorganic ions and organic compounds, could impact the ion exchange efficiency of phosphate with the resin and reduce the removal rate. The results were consistent with previous report [33,34].

3.2. Effects of pH and competing anions on phosphorous removal

Fig. 2 shows the variations of Q_e of phosphate with the co-existence of Cl^- , NO_3^- , and SO_4^{2-} at different pH. For all kinds of anions, Q_e initially increased with increasing pH, and then decreased once the pH rose above 10. The maximal Q_e was obtained at pH 10. It was observed that with the existence of competing anions, Q_e of phosphate was reduced, and the effect of SO_4^{2-} was most significant, which is consistent with Helfferich's electrosensitivity concept [35]. The higher ionic valence facilitated the sorption of ions onto ion exchange resins, and thus selectivity of the resin was higher.

The ion exchange process between resin and phosphate could be expressed as following:



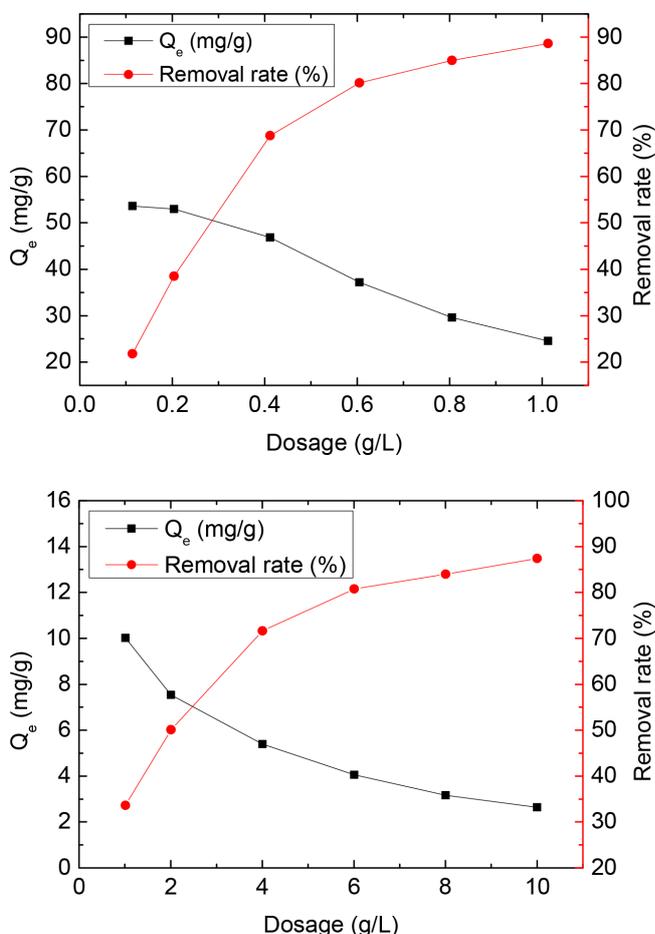


Fig. 1. Variations of Q_e and removal rate of phosphate by resin as functions of resin dosage in (a) synthetic wastewater and (b) real wastewater. All samples were collected after oscillation in a vibrator at 298 K and 120 rpm for 24 h at pH 10.

where R^{n+} is the cation group of ion exchange resin; n is the number of ionic valence; and j is the number of released H^+ . Since the acid dissociation constants of phosphoric acid in aqueous solution are $pK_{a1} = 2.16$, $pK_{a2} = 7.21$, and $pK_{a3} = 12.32$ [36]. Phosphorus mainly exists as $H_2PO_4^-$ in the range of pH 2–7, and switches to HPO_4^{2-} when pH increases to 7–12 [37]. In this study, with increasing pH, phosphorus was gradually transformed from $H_2PO_4^-$ to HPO_4^{2-} , and the Eq. (3) could be read as following:



According to Helfferich's electrosensitivity concept, the selectivity of resin with HPO_4^{2-} was higher than that of $H_2PO_4^-$, which could accelerate the reaction rate from left to

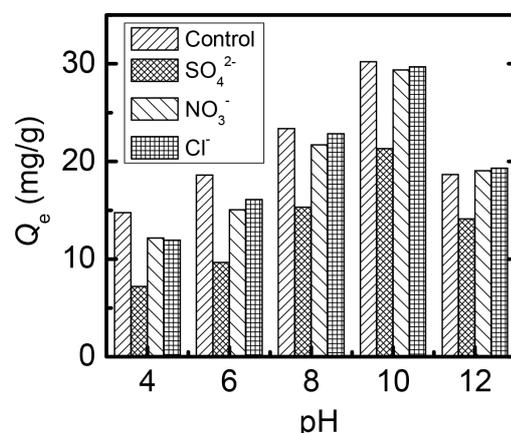


Fig. 2. Effects of pH and competing anions on Q_e of the Amberlite IRA-958 resin. The initial concentration of competing anions is 290 mM, which was the equivalent molar concentration of PO_4^{3-} . All the conical flasks were set in a vibrator to oscillate at 120 rpm and 298 K after the addition of 1.0 g/L resin for 24 h.

right of Eq. (3). Moreover, with the increase of pH, the concentration of dissociative H^+ became lower, promoting the right-shift of Eq. (3), and thus enhanced the removal efficiency of phosphate. However, with the further increase of pH ($pH > 10$), the acid dissociation constants of phosphoric acid was too low to delay the ion exchange process. Therefore, the ion exchange capability of resin was reduced when the pH was higher than 10.

According to Eq. (3), the existence of Cl^- in the solution could induce a left-shift of the equilibrium of the equation, which resulted in a reduction of the amount of phosphate sorbed. SO_4^{2-} and NO_3^- could compete with phosphate to the ion exchange sites and reduce the removal rate of phosphate. Q_e of phosphate in all the solution was reduced when pH reached 12, suggesting that the increased OH^- competed with phosphate and reduced its removal rate.

3.3. Mechanisms of phosphate removal by ion exchange resin

The variation of sorption capacity of phosphate onto Amberlite IRA-958 resin with contact time is displayed in Fig. 3. With dosage of 1.0 g/L resin, the sorption capacity of phosphate in synthetic wastewater was 23.1 mg/g (resin), while that in real wastewater (AnMBR effluent) was 8.5 mg/g (resin). For both synthetic and real wastewater, the sorption capacity increased with extension of contact time during the initial sorption, and the increasing rate of sorption capacity in synthetic wastewater was higher than that in real wastewater. For synthetic wastewater, the sorption capacity was almost stable after 360 min of contact, which was considered to have reached the sorption equilibrium. However, with real wastewater, the increase in the sorption capacity reached a plateau after 150 min of reaction time, and then the sorption equilibrium was reached. The results indicate that the ion exchange resin exhibited greater phosphate removal capacity in synthetic wastewater than in real wastewater, which was probably mainly due to the complex composition of real wastewater.

On the basis of results of this study, the competing anions existent in the real wastewater and solution chemistry (pH) showed significant effects on the removal efficiency of phosphorus by ion exchange resin. Therefore, the pretreatment of real wastewater, such as the removal of high valent anions via precipitation method and adjustment of pH condition, is necessary to improve the ion exchange efficiency of phosphorus.

3.3.1. Sorption kinetics model

The following pseudo-first order model equation (Eq. 4) and pseudo-second order model equation (Eq. 5) were used to simulate phosphate sorption kinetics on the resin [38].

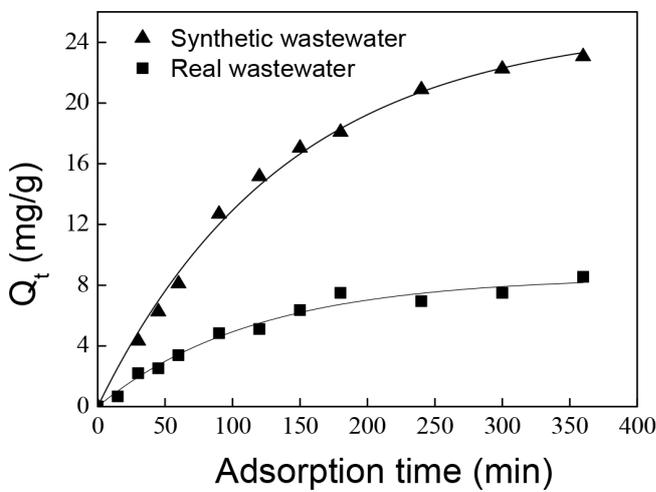


Fig. 3. Effects of contact time on phosphate adsorption onto Amberlite IRA-958 resin. The dosage of resin was 1.0 g/L, and the beakers were oscillated in a vibrator at 120 rpm and 298 K.

$$\log(Q_e - Q_t) = \log(Q_e) - \frac{K_{ad}}{2.303}t \tag{4}$$

$$\frac{t}{Q_t} = \frac{1}{K_t Q_e^2} + \frac{t}{Q_e} \frac{t}{Q_t} = \frac{1}{K_t Q_e^2} + \frac{t}{Q_e} \tag{5}$$

where, Q_t is the phosphate sorption capacity of resin at the time of t (mg/g); Q_e is the phosphate sorption capacity of resin at the moment of sorption equilibrium (mg/g); K_{ad} is the constant of the first-order model sorption (min^{-1}); and K_t is the diffusion constant in particles (min^{-1}).

The simulated results are demonstrated in Fig. 4 and Table 2. They show that R^2 values of fitting the data to the pseudo-first order equation were higher than that of the pseudo-second order equation. Therefore, the phosphate sorption kinetics on the resin corresponded more to the pseudo-first order model. Moreover, the Q_e values calculated by the pseudo-first order model were 26.6 mg/g and 7.7 mg/g in synthetic wastewater and real wastewater, which was similar to the experimental results of 23.1 mg/g and 8.5 mg/g in synthetic wastewater and real wastewater, respectively. The results indicate that the equilibrium sorption capacity calculated by simulating the pseudo-first order model exhibited greater accordance with the experimental data (Table 2). Thus, phosphate sorption onto Amberlite IRA-958 resin from both real wastewater and synthetic wastewater corresponded with the pseudo-first order model.

3.3.2. Determination of the rate-limiting step

The boundary model has been widely applied to describe the sorption behavior of porous materials [39,40]. The phosphate removal process by ion exchange resin from wastewater can be divided into three steps: 1) diffusion of phosphate from the solution through liquid film to the

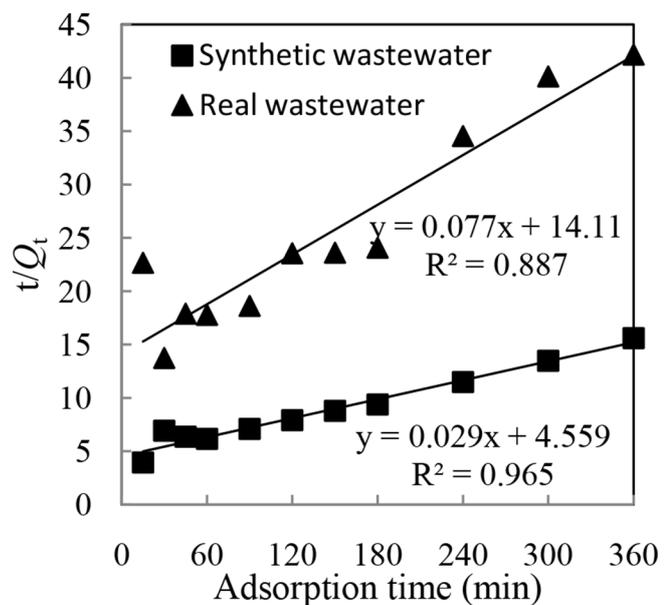
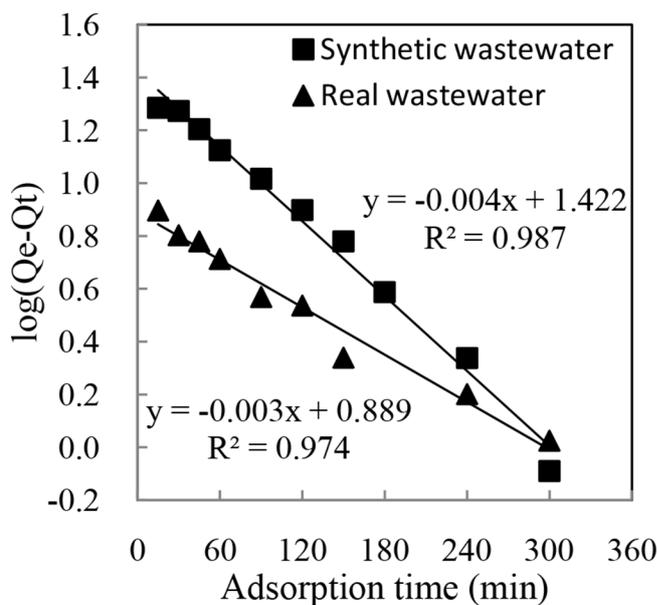


Fig. 4. Linear simulation of (a) pseudo-first order model and (b) pseudo-second order model

Table 2
Kinetic model parameters of phosphate adsorption on Amberlite IRA-958 resin*

Samples	$Q_{e,exp}/(\text{mg}\cdot\text{g}^{-1})$	First-order adsorption rate model		Second-order adsorption rate model	
		$Q_{e,cal}/(\text{mg}\cdot\text{g}^{-1})$	$K_{ad}/(\text{min}^{-1})$	$Q_{e,cal}/(\text{mg}\cdot\text{g}^{-1})$	$K_t/(\text{min}^{-1})$
Synthetic waste-water	23.1	26.5	1.1E-02	33.8	1.9E-04
Real wastewater	8.5	7.7	6.9E-03	12.9	4.3E-04

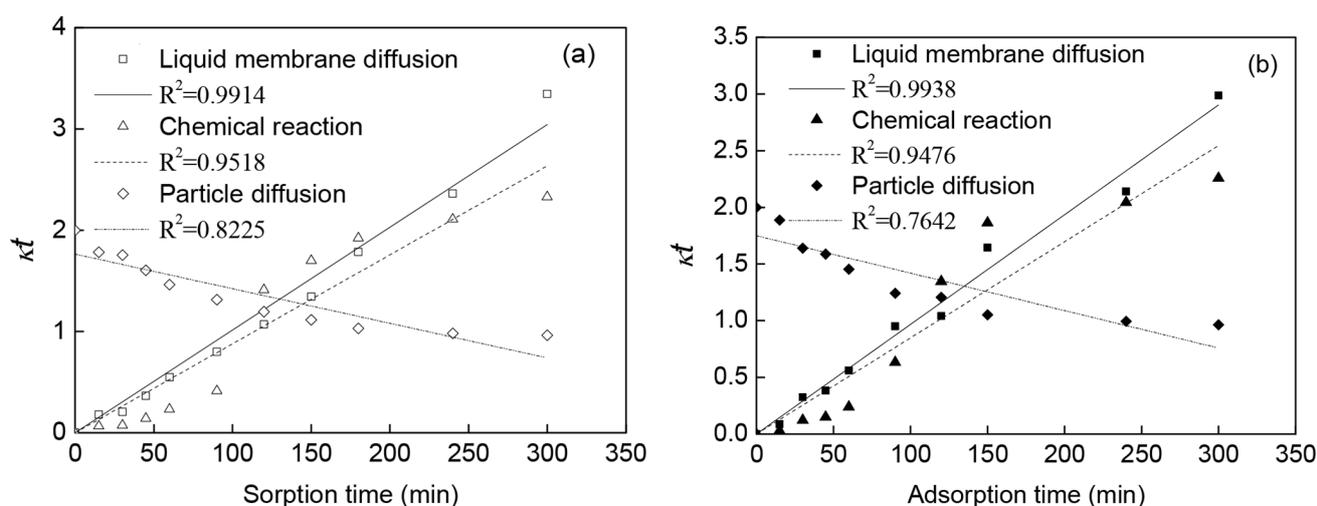


Fig. 5. Simulation of boundary model of (a) synthetic wastewater and (b) real wastewater.

surface of ion exchange resin; 2) diffusion of phosphate from the surface of ion exchange resin to the interior; 3) reaction between phosphate and the active groups in the ion exchange resin. Therefore, the ion exchange process of phosphate can be affected by the speed of these three steps, i.e. liquid film diffusion, particle diffusion, and chemical reaction, among which the slowest step will be the rate-limiting step.

The equations of membrane diffusion (Eq. 6), particle diffusion (Eq. 7) and chemical reaction (Eq. 8) from the boundary model can be expressed as follows [41]:

$$-\ln(1-F) = kt \quad (6)$$

$$1 - 3(1-F)^{2/3} + 2(1-F) = kt \quad (7)$$

$$1 - (1-F)^{1/3} = kt \quad (8)$$

where $F (Q_t/Q_e)$ is the degree of ion exchange and indicates the sorption fraction at the moment of t , and k is the velocity constant.

The experimental data shown in Fig. 5 was adopted to simulate the sorption kinetics using these boundary model equations. The data indicates that the goodness of fit of liquid film diffusion (0.9914, 0.9938) was higher than that of particle diffusion (0.8225, 0.7642) and chemical reaction (0.9518, 0.9476). Thus, liquid film diffusion was considered

to be the limiting step for phosphate sorption from both real wastewater and synthetic wastewater. The effects of speed on the ion exchange efficiency can be found in our previous report [32].

3.3.3. Isothermal sorption model

The isothermal sorption simulation results shown in Fig. 2 was carried out using the Langmuir equation (Eq. 9) and Freundlich equation (Eq. 10) as follows [38]:

$$\frac{C_e}{Q} = \frac{C_e}{Q_m} + \frac{1}{Q_m} b \quad (9)$$

$$\ln Q_e = \left(\frac{1}{n}\right) \ln C_e + \ln K_F \quad (10)$$

where Q_m is the maximum sorption capacity, b is the Langmuir constant, and n and K_F are the Freundlich constant. A Freundlich constant (n) in the range of 2 to 10 implies that the sorption is apt to happen, while if n is less than 0.5, the sorption process is difficult.

The simulated results (Table 3) indicate that phosphate in synthetic wastewater was more easily sorbed onto Amberlite IRA-958 resin than that of real wastewater. The phosphate sorption of Amberlite IRA-958 resin in real wastewater was situated between the favorable and unfavorable sorption. By comparing the linear correlation

Table 3
Simulating results of Langmuir model and Freundlich model*

Samples	Langmuir model			Freundlich model		
	Q_m (mg·g ⁻¹)	b (L·mg ⁻¹)	R^2	n	K_F	R^2
Synthetic wastewater	66.7	0.694	0.9920	2.52	27.74	0.91
Real wastewater	25.6	0.101	0.9127	1.29	2.46	0.990

* Q_m is the saturated sorption amount, b is the Langmuir constant, and n and K_F are the Freundlich constant.

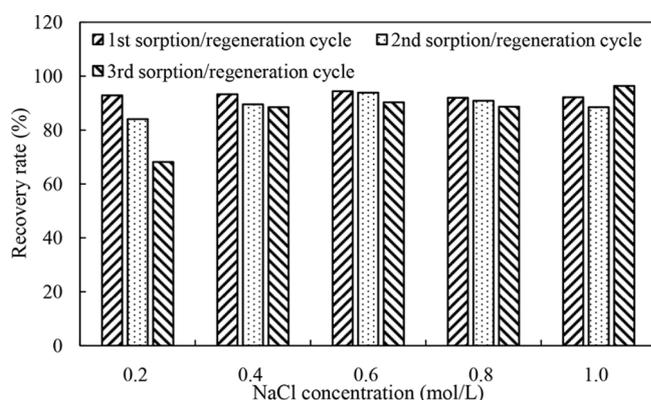


Fig. 6. Effects of regeneration solution on the Q_e (sorption/regeneration cycles = 3).

coefficients of the two fitted models, phosphate sorption in synthetic wastewater aligned with Langmuir isothermal sorption, and was considered as monolayer sorption. With real wastewater, the sorption of phosphate aligned better with Freundlich isothermal sorption, and the fitting goodness was more than 0.99. Due to the complicated composition of real wastewater, the sorption behavior of resin in real wastewater was different from that in synthetic wastewater.

3.4. Regeneration experiments

The effects of NaCl concentration on the recovery rate of Q_e of phosphate are shown in Fig. 6. For the first cycle, the recovery rate at all the NaCl concentrations showed similar values (ca. 85%). However, when 0.2 mol/L NaCl was used as regeneration solution, the recovery rate of phosphate gradually reduced as time progressed, indicated that phosphate was not completely removed by the regeneration operation. When the NaCl concentration was higher than 0.2 mol/L, the sorption capacity of phosphate was generally stable for all the regeneration cycles. The average amount of phosphate in the eluant and residual on the resin of three cycles regenerated with different NaCl concentration were calculated basis on the mass balance. The average amount of phosphate residual on the resin was 0.36, 0.31, 0.30, 0.30 and 0.29 mg by using the regeneration solution containing 0.2, 0.4, 0.6, 0.8 and 1.0 mol/L NaCl, respectively. To minimize the cost of regeneration during practical application of ion exchange resin, 0.4 mol/L NaCl was considered as

the optimal concentration of regeneration solution, based on the results of current study.

4. Conclusions

In this study, the mechanisms of phosphorus removal from both synthetic wastewater and real wastewater using ion exchange resin were investigated. The results showed that the sorption capacity of phosphate by Amberlite IR-958 in synthetic wastewater was much higher than that in real wastewater (i.e. effluent of AnMBR). The phosphate sorption capacity of Amberlite IRA-958 resin used in this study was compared with the previous study [42]. Martin et al. [42] compared the sorption capacity for phosphate of a hybrid anion exchanger (HAIX) with ferric oxide nanoparticles and Amberlite IRA-410 resin. The sorption capacity of HAIX was 23.55 mg/g from a solution with an initial concentration of 15.2 mg/L. In contrast, Amberlite IRA-410 removed only 0.99 mg PO_4^{3-} per gram resin from a solution with an initial concentration of 16.2 mg/L. Compared to their results, the phosphate sorption capacity of Amberlite IRA-958 resin in this study was relatively high, which supports its use as a robust ion exchange material for phosphorus removal.

The existence of competing anions could reduce the removal rate of phosphorus, and the effects of SO_4^{2-} were most significant. The kinetics of the ion exchange process between phosphate and the ion exchange resin (Amberlite IRA-958) in both real wastewater and synthetic wastewater were in accordance with the pseudo-first order kinetic model. Liquid film diffusion was the rate-limiting step for phosphate sorption. The sorption behavior of the resin in synthetic wastewater fit better with Langmuir isothermal sorption, while the sorption behavior in real wastewater was consistent with Freundlich isothermal sorption. Because of the complicated composition of real wastewater, the sorption behavior of resin was different from that in synthetic wastewater. The solution with 0.4 mol/L NaCl could be used as the regeneration solution of the Amberlite IRA-958 resin.

On the basis of the results of this study, the utilization of ion exchange method for phosphorus recovery is feasible, even though the some pretreatment of real wastewater was needed to improve the sorption efficiency. Furthermore, the phosphorus recovered from ion exchange process is highly purity due to the selectivity of ion exchange resin. Therefore, it is a future perspective to produce the highly purified struvite as agricultural fertilizer for achieving sustainable development of phosphorus.

Symbols

n	—	Freundlich constant
b	—	Langmuir constant
C_e	—	Equilibrium phosphate concentrations in the solution (mg/L)
C_o	—	Initial phosphate concentrations in the solution (mg/L)
$F (Q_t/Q_e)$	—	ion exchange degree
k	—	Velocity constant
K_{ad}	—	Constant of the first-order model sorption (min^{-1})
K_F	—	Freundlich constant
K_t	—	Diffusion constant in particles (min^{-1})
m	—	Mass of the resin (g)
Q_e	—	Equilibrium sorption capacity of phosphate (mg/g)
Q_m	—	Maximum sorption capacity (mg/g)
Q_t	—	Phosphate sorption capacity of resin at the time of t (mg/g)
V	—	Solution volume (L)
η	—	Moisture (%)

Acknowledgements

This research was funded by National Natural Science Foundation of China (51308400), and the Foundation of State Key Laboratory of Pollution Control and Resource Reuse (Tongji University), China (PCRRE16003 & PCRRY14002).

References

- [1] R.J. Seviour, T. Mino, M. Onuki, The microbiology of biological phosphorus removal in activated sludge systems, *FEMS Microbiol. Rev.*, 27 (2003) 99–127.
- [2] A.N. Sharpley, Agricultural phosphorus and eutrophication, *J. Environ. Qual.*, 27 (1998) 251–257.
- [3] T.D. Mccobb, D.R. Leblanc, D.A. Walter, K.M. Hess, D.B. Kent, R.L. Smith, Phosphorus in a ground-water contaminant plume discharging to Ashumet Pond, Cape Cod, Massachusetts, 1999, Water-Resources Investigations Report (2003).
- [4] L. Jin, G. Zhang, H. Tian, Current state of sewage treatment in China, *Water Res.*, 66 (2014) 85–98.
- [5] H. Yoshida, W.A. Galinada, Equilibria for adsorption of phosphates on OH-type strongly basic ion exchanger, *AIChE J.*, 48 (2002) 2193–2202.
- [6] D. Cordell, J.O. Drangert, S. White, The story of phosphorus: Global food security and food for thought, *Global Environ. Change*, 19 (2009) 292–305.
- [7] D. Cordell, T.S.S. Neset, Phosphorus vulnerability: A qualitative framework for assessing the vulnerability of national and regional food systems to the multi-dimensional stressors of phosphorus scarcity, *Global Environ. Change.*, 24 (2013) 108–122.
- [8] L. Reijnders, Phosphorus resources, their depletion and conservation, a review, *Resour. Conserv. Recycl.*, 93 (2014) 32–49.
- [9] D.P.V. Vuuren, A.F. Bouwman, A.H.W. Beusen, Phosphorus demand for the 1970–2100 period: A scenario analysis of resource depletion, *Global Environ. Change*, 20 (2010) 428–439.
- [10] Z. Yuan, S. Pratt, D.J. Batstone, Phosphorus recovery from wastewater through microbial processes, *Curr. Opin. Biotechnol.*, 23 (2012) 878–883.
- [11] T. Nur, P. Loganathan, J. Kandasamy, S. Vigneswaran, Phosphate adsorption from membrane bioreactor effluent using Dowex 21K XLT and recovery as Struvite and Hydroxyapatite, *Int. J. Environ. Res. Public Health*, 13 (2016).
- [12] E. Desmidt, K. Ghyselbrecht, Y. Zhang, L. Pinoy, B. Van der Bruggen, W. Verstraete, K. Rabaey, B. Meesschaert, Global Phosphorus scarcity and full-scale P-recovery techniques: A review, *Crit. Rev. Environ. Sci. Technol.*, 45 (2015) 336–384.
- [13] Z. Xie, Z. Wang, Q. Wang, C. Zhu, Z. Wu, An anaerobic dynamic membrane bioreactor (AnDMBR) for landfill leachate treatment: Performance and microbial community identification, *Bioresour. Technol.*, 161 (2014) 29–39.
- [14] H. Lin, W. Peng, M. Zhang, J. Chen, H. Hong, Y. Zhang, A review on anaerobic membrane bioreactors: Applications, membrane fouling and future perspectives, *Desalination*, 314 (2013) 169–188.
- [15] A.L. Smith, L.B. Stadler, N.G. Love, S.J. Skerlos, L. Raskin, Perspectives on anaerobic membrane bioreactor treatment of domestic wastewater: A critical review, *Bioresour. Technol.*, 122 (2012) 149–159.
- [16] S. Aiyuk, J. Amoako, L. Raskin, A. van Haandel, W. Verstraete, Removal of carbon and nutrients from domestic wastewater using a low investment, integrated treatment concept, *Water Res.*, 38 (2004) 3031–3042.
- [17] M.A.H. Johir, J. George, S. Vigneswaran, J. Kandasamy, A. Grasmick, Removal and recovery of nutrients by ion exchange from high rate membrane bio-reactor (MBR) effluent, *Desalination*, 275 (2011) 197–202.
- [18] Ö. Aydın, C. Özmetin, M. Korkmaz, B.A. Fil, A semi-empirical kinetic model for removal of Iron (Fe^{3+}) from saturated Boric Acid solution by ion exchange using Amberlite IR-120 Resin, *Part. Sci. Technol.*, (2015) 1–7.
- [19] B.A. Fil, A.E. Yilmaz, R. Boncukcuoğlu, S. Bayar, Removal of divalent heavy metal ions from aqueous solution by Dowex HCR-S synthetic resin, *Bulg. Chem. Commun.*, 44 (2012) 201–207.
- [20] M.R. Awual, A. Jyo, Assessing of phosphorus removal by polymeric anion exchangers, *Desalination*, 281 (2011) 111–117.
- [21] B. Saha, S. Chakraborty, G. Das, A mechanistic insight into enhanced and selective phosphate adsorption on a coated carboxylated surface, *J. Colloid Interface Sci.*, 331 (2009) 21–26.
- [22] I. Midorikawa, H. Aoki, A. Omori, T. Shimizu, Y. Kawaguchi, K. Kassai, T. Murakami, Recovery of high purity phosphorus from municipal wastewater secondary effluent by a high-speed adsorbent, *Water Sci. Technol.*, 58 (2008) 1601–1607.
- [23] M. Zarrabi, M.M. Soori, M.N. Sepehr, A. Amrane, S. Borji, H.R. Ghaffari, Removal of phosphorus by ion-exchange resins: equilibrium, kinetic and thermodynamic studies, *Environ. Eng. Manag. J.*, 13 (2014) 891–903.
- [24] R. Karunanithi, A.A. Szogi, N. Bolan, R. Naidu, P. Loganathan, P.G. Hunt, M.B. Vanotti, C.P. Saint, S.O. Yong, S. Krishnamoorthy, Phosphorus recovery and reuse from waste streams, *Adv. Agron.*, 131 (2015) 173–250.
- [25] A. Pintar, J. Batista, J. Levec, Integrated ion exchange/catalytic process for efficient removal of nitrates from drinking water, *Chem. Eng. Sci.*, 56 (2001) 1551–1559.
- [26] S. Liang, M.A. Mann, G.A. Guter, H.S. Kim, D.L. Hardan, Nitrate removal from contaminated groundwater, *J. AWWA.*, 91 (1999) 79–91.
- [27] S. Samatya, N. Kabay, Ü. Yüksel, M. Arda, M. Yüksel, Removal of nitrate from aqueous solution by nitrate selective ion exchange resins, *React. Funct. Polym.*, 66 (2006) 1206–1214.
- [28] L. Bulgariu, A. Ceica, L. Lazar, I. Cretescu, I. Balasanian, Equilibrium and Kinetics Study of Nitrate Removal from Water by Purolite A100 Resin, *Revista de Chimie -Bucharest- Original Edition-* 11 (2010) 1136–1141.
- [29] O. Primo, M.J. Rivero, A.M. Urriaga, I. Ortiz, Nitrate removal from electro-oxidized landfill leachate by ion exchange, *J. Hazard. Mater.*, 164 (2009) 389–393.
- [30] T. Nur, M.A.H. Johir, P. Loganathan, S. Vigneswaran, J. Kandasamy, Effectiveness of purolite A500PS and A520E ion exchange resins on the removal of nitrate and phosphate from synthetic water, *Desal. Water Treat.*, 47 (2012) 50–58.
- [31] W.G. Walter, APHA Standard Methods for the Examination of Water and Wastewater, *Am. J. Public Health & Nations Health* (1961).

- [32] C. Liu, Q. Wang, F. Huang, J. Zhang, Removal of phosphorus from anaerobic membrane bioreactor effluent by ion exchange resin, *Sep. Sci. Technol.*, (2016).
- [33] A.T.K. Tran, Y. Zhang, J. Lin, P. Mondal, W. Ye, B. Meesschaert, L. Pinoy, B. Van der Bruggen, Phosphate pre-concentration from municipal wastewater by electrodialysis: Effect of competing components, *Sep. Purif. Technol.*, 141 (2015) 38–47.
- [34] L.M. Blaney, S. Cinar, A.K. Sengupta, Hybrid anion exchanger for trace phosphate removal from water and wastewater, *Water Res.*, 41 (2007) 1603–1613.
- [35] H.F. Walton, Ion exchange, *Anal. Chem.*, 44 (1972) 256–270.
- [36] C. Furlani, Complexation in analytical chemistry, *J. Chromatogr. A*, 16 (1964) 268–268.
- [37] J.P. Chen, M.L. Chua, B. Zhang, Effects of competitive ions, humic acid, and pH on removal of ammonium and phosphorous from the synthetic industrial effluent by ion exchange resins, *Waste Manage. (Oxford)*, 22 (2002) 711–719.
- [38] T. Nur, M.A.H. Johir, P. Loganathan, S. Vigneswaran, J. Kandasamy, Effectiveness of purolite A500PS and A520E ion exchange resins on the removal of nitrate and phosphate from synthetic water, *Desal. Water Treat.*, 7 (2012) 50–58.
- [39] M.A.B. Altamirano, S. Cordero, R. Lopez-Esparza, E. Perez, A.G. Goicochea, Importance of pore length and geometry in the adsorption/desorption process: a molecular simulation study, *Mol. Phys.*, 113 (2015) 3849–3853.
- [40] M. Rutigliano, N. Sanna, A. Palma, Multiple approach to model unpaired spin density effects in H-ZSM5 zeolite with extra-framework O atom: H-abstraction reaction from methane, *Comput. Theor. Chem.*, 1074 (2015) 9–18.
- [41] F.G. Helfferich, Ion exchange, Courier Corporation, 1962.
- [42] B.D. Martin, S.A. Parsons, B. Jefferson, Removal and recovery of phosphate from municipal wastewaters using a polymeric anion exchanger bound with hydrated ferric oxide nanoparticles, *Water Sci. Technol.*, 60 (2009) 2637–2645.