



## Effectiveness of purolite A500PS and A520E ion exchange resins on the removal of nitrate and phosphate from synthetic water

T. Nur, M.A.H. Johir, P. Loganathan, S. Vigneswaran\*, J. Kandasamy

*Faculty of Engineering and Information Technology, University of Technology, Broadway, Sydney, NSW 2007, Australia*

*Email: s.vigneswaran@uts.edu.au*

Received 25 August 2011; Accepted 6 February 2012

### ABSTRACT

Water pollution due to the excessive presence of nutrients (nitrogen and phosphorus) is a serious environmental worldwide problem, because both species are implicated in the eutrophication of receiving surface waters and elevated nitrate concentration in drinking water can be toxic to infants. The removal efficiencies of nitrate and phosphate from water spiked with different ratios and concentrations of these nutrients by two ion-exchange resins (Purolite A500PS and Purolite A520E) were studied in batch kinetics and equilibrium adsorption experiments. Both purolites were found to be selective towards nitrate removal at all ratios of nitrate to phosphate in solution. Purolite A520E showed higher (<85%) removal efficiency of nitrate than Purolite A500PS (about 65%) from a solution containing 20 mg N/L as nitrate and 10 mg P/L as phosphate at a resin dose of 1.5 g/L. However, Purolite A500PS showed higher (65%) removal of phosphate than Purolite A520E (48%). Langmuir and Freundlich isotherm models fitted well for the adsorption of nitrate on Purolite A520E ( $R^2 = 0.95\text{--}0.96$ ). However, the adsorption of nitrate on Purolite A500PS can be explained satisfactorily only by Freundlich model ( $R^2 = 0.98$ ). The adsorption of phosphate on the resins fitted well to Freundlich model ( $R^2 = 0.90$ ) for Purolite A500PS as well as for Purolite A520E ( $R^2 = 0.90$ ). The adsorption of phosphate and nitrate on both ion-exchange resins was much better described by pseudo-second-order kinetic model ( $R^2 \geq 0.99$ ) than by pseudo-first-order kinetic model ( $R^2 = 0.25\text{--}0.94$ ).

*Keywords:* Purolite; Ion-exchange resin; Nitrate; Phosphate; Adsorption isotherm and kinetics

### 1. Introduction

Recently, reclamation and reuse of treated wastewaters have received great interest because of severe water shortage in many countries. As the global supplies of clean water diminish and demand for the water rises, advanced wastewater treatment is becoming an international focus for the rational use of scarce

water resources and as means of safeguarding aquatic environments from the harm caused by wastewater disposal. Nutrients such as nitrogen (N) and phosphorous (P) are the major pollutant discharges from municipal, industrial and agricultural wastewaters. These pollutant discharges afterwards mix into water resources. Throughout recent decades, the wastewater treatment industry has identified the discharge of nutrients, including phosphates and nitrates, into

\*Corresponding author.

waterways as a risk to natural environments due to the serious effects of eutrophication [1]. Eutrophication is the abundance of aquatic plants, growth of algae and depletion of dissolved oxygen [2]. To alleviate the environmental impact of these eutrophic enhancers, novel technologies have been aggressively sought to reduce effluent P and N concentrations of both industrial and domestic wastewater. Furthermore, the presence of nitrate ions in drinking water is a potential public health hazard including infant methaemoglobinemia (“blue baby” syndrome) [3,4]. Therefore, nitrate and phosphate removal is essential in wastewater treatment and for potential reuse of the treated water. On the other hand, the nutrients can be removed from the wastewater by adsorption on ion-exchange materials and can be recovered and used as fertilizer. This process will help to reduce nutrient load in the receiving water body, and at the same time, the recovered nutrients will also act as a fertilizer when applied to crops.

Several physicochemical and biological processes have been investigated for the removal of dissolved nutrients in water and wastewaters. The methods available for the removal of nitrate and phosphate are ion exchange [5–8], biological denitrification [9,10], catalytic reduction [11,12], reverse osmosis [13] and electrodialysis [14–16]. However, the application of these processes has been limited as they are relatively expensive and merely displace nitrate into concentrated waste brine that may pose a disposal problem [10]. The advantage of a catalytic reduction process is the rapid removal of nitrate from water [12,16]. The disadvantage of this process is its high capital cost. Phosphorus can also be removed by biological processes. Although this process is environment-friendly, one cannot remove phosphorous below a particular concentration if there is a lack of easily biodegradable organic carbon present in the wastewater.

Among the various methods of nutrient removal, adsorption/ion-exchange methods are promising, because they allow simple and economical operation, resulting in less sludge production and therefore minimal disposal problems. Furthermore, these methods seem to be the most suitable for small water supplies contaminated by nutrients because of its simplicity, effectiveness, selectivity, recovery and relatively low cost [6,7]. These methods also have the ability to handle shock loadings and the ability to operate over a wide range of temperatures. Several materials such as fly ash, cement, surfactant-modified zeolite, alunite, polymeric ion exchangers and agricultural residues have been investigated as adsorbents for the removal of phosphate and/or nitrate anions [17–21]. However, these materials exhibited insuffi-

cient adsorption and regeneration capacities, as well as poor selectivity.

A variety of adsorbents have been used for selectively removing nitrate, such as Purolite A520E [22], Purolite A100 [23], Purolite A520E and Purolite A300 [24], macroreticulated Amberlite IRA900 [25] and Dowex SBRP [26]. A variety of adsorbents have also been developed for selectively removing phosphate, such as aluminium oxide, iron oxide, zirconium oxide, ion-exchange resin, hydrotalcite [27] and layered double hydroxides [28].

Nitrate-specific resins have been proven to have affinity for the following ions in decreasing order:  $\text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^-$  [29]. Several ion-exchange resins were used for nitrate removal from drinking water. The characteristics of adsorption behaviour on resins are generally inferred in terms of both adsorption kinetics and equilibrium isotherms. Samatya et al. [22] used the ion-exchange resin Purolite A520E to remove nitrate from water and found that this resin gave promising results for column-mode removal of nitrate from ground water. By fitting their data to Langmuir adsorption isotherm, they reported the maximum adsorption value of 18.5 mg N/g dry resin and energy of sorption value of 0.4 L/mg. Bulgariu et al. [23] reported a lower maximum uptake capacity of 19.38 mg N/g resins for nitrate adsorption on Purolite A100. Removal of nitrate from aqueous solutions was studied using two nitrate-selective anion exchangers Purolite A520E and Purolite A300 under a fixed bed configuration by Primo et al. [24], and it was found that Purolite A300 showed a higher removal efficiency of nitrate than Purolite A520E.

The methods currently available for the removal of nitrate and phosphate by ion exchangers are specific only for one of these nutrients. Purolite as an adsorbent has been studied to remove nitrate and not phosphate except in a very recent study by Johir et al. [30] where the removal of nitrate and phosphate from wastewater was tested with Purolite A520E and A500PS in ion-exchange columns in series. They found that 40% and 80% of phosphates were removed by Purolite A520E and Purolite A500PS, respectively, whereas a higher percentage (80–95%) of nitrate was removed by both resins. Most of the previous studies have not considered the effect of purolite on simultaneous removal of both nitrate and phosphate. The effects of different concentrations and ratios of nitrate to phosphate on their removal by purolite were also not investigated in previous studies.

The present work is intended to study the effectiveness of the ion-exchange resins (Purolite A520E and Purolite A500PS) to remove nitrate and phosphate from wastewater. The objectives of this study were

divided into two parts: (i) investigation of the competitive adsorption of nitrate and phosphate when they are present at different concentration ratios in synthetic water and (ii) study of kinetic and equilibrium adsorption isotherms of nitrate or phosphate adsorption on these ion-exchange resins.

## 2. Material and methods

### 2.1. Ion-exchange resins

Two ion-exchange resins, namely Purolite A520E and Purolite A500PS, were used as adsorbents. The Purolite A520E is a macroporous strong base anion resin, which is specially designed for the removal of nitrates from water for potable purposes [31]. Purolite A500PS is designed for use as an organic scavenger, for example for the removal of tannins, fulvic and humic acids, from domestic effluents [31]. It was found to have a good phosphate ion-exchange capacity [30]. The macroporous matrix and special ion-exchange group functionality impart ideal selectivity to nitrate and phosphate. The characteristics of these ion-exchange resins are presented in Table 1.

### 2.2. Feed solution

The feed solution was distilled water spiked with nitrate and phosphate. Solutions with different con-

centrations of nitrate (10–50 mg N/L) and phosphate (2–20 mg P/L) were prepared using  $\text{KNO}_3$  and  $\text{KH}_2\text{PO}_4$ .

### 2.3. Chemical analysis

The analyses of nitrate and phosphate ions were carried out using Metrohm ion chromatograph (model 790 Personal IC) equipped with an autosampler and conductivity cell detector. The separation was achieved using an A SUPP column 3 (150 × 4 mm).  $\text{Na}_2\text{CO}_3$  (3.2 mmol/L) and  $\text{NaHCO}_3$  (1.0 mmol/L) were used as a mobile phase with a flow rate of 0.9 mL/min.

### 2.4. Batch adsorption isotherm studies

Isotherm experiments were conducted in a set of glass flasks with 100 mL solutions spiked with nutrients (10 mg P/L and 20 mg N/L) and different ion-exchange resin concentrations of 0.1–10 g/L at room temperature ( $24 \pm 1^\circ\text{C}$ ). The suspensions were agitated in a flat shaker at a shaking speed of 120 rpm for 72 h to ensure that the adsorption equilibrium is reached. However, preliminary experiments showed that the adsorption equilibrium was achieved within 48 h. The experiments were duplicated to achieve minimal difference in adsorption between the duplicates. The amount of adsorption at equilibrium,  $q_e$  (mg/g), was calculated by the Eq. (1),

Table 1  
Typical chemical and physical characteristics of the two purolites used [31]

Parameters	A500PS	A520E
Polymer matrix structure	Macroporous polystyrene cross-linked divinylbenzene	Macroporous styrene-divinylbenzene
Physical form and appearance	Spherical beads	Opaque cream spherical beads
Functional groups	R-(Me) <sub>3</sub> N <sup>+</sup>	Quaternary Ammonium
Ionic form (as shipped)	Cl <sup>-</sup>	Cl <sup>-</sup>
Screen size range (US standard screen)	16–40 mesh, wet	16–50 mesh, wet
Particle size range (microns)	+1,200 < 2%, -420 < 2%	+1,200 < 5%, -300 < 1%
Moisture retention, Cl <sup>-</sup> form	63–70%	50–56%
Reversible swelling Cl <sup>-</sup> ® OH (SO <sub>4</sub> /NO <sub>3</sub> )	20% max (-)	Negligible
Specific gravity (Cl <sup>-</sup> form)	1.04	-
Total exchange capacity, Cl <sup>-</sup> form		
Wet, volumetric	0.8 eq/l min	0.9 eq/l min
Dry, weight	-	2.8 meq/g min
pH range (stability), Cl <sup>-</sup> Form	0–14	0–14
Operating temperature(Cl <sup>-</sup> form)	100°C	100°C

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where  $C_0$  is the initial concentration of adsorbate (mg/L);  $C_e$  is the equilibrium concentration of the adsorbate (mg/L);  $V$  is the volume of the solution (L); and  $M$  is the mass of adsorbent used (g).

The experimental results were treated with both Langmuir and Freundlich isotherm models. The equations for Langmuir and Freundlich isotherms are presented in Table 2.

### 2.5. Batch adsorption kinetic studies

The batch adsorption kinetic experiments were conducted with different concentrations of ion-exchange resins with various adsorbate concentrations (nitrate and phosphate) in a glass flask containing 100 mL of adsorbate solution and agitated in a flat shaker at a shaking speed of 120 rpm for 4 h. The aqueous samples were taken at different time intervals, and the concentrations of nitrate and phosphate were measured. The amount of adsorption at time  $t$ ,  $q_t$  (mg/g), was calculated by Eq. (2):

$$q_t = \frac{(C_0 - C_t)V}{M} \tag{2}$$

where  $C_0$  is the initial concentration of adsorbate (mg/L);  $C_t$  is the concentration of adsorbate at time  $t$  (mg/L);  $V$  is the volume of the solution (L); and  $M$  is the mass of the dry adsorbent used (g).

The adsorption kinetic data were analysed by pseudo-first-order and pseudo-second-order kinetic models. The equations for pseudo-first-order and pseudo-second-order kinetic models are presented in Table 2.

## 3. Results and discussion

### 3.1. Comparison between the two purolites in removing nitrate and phosphate

The batch kinetic experimental results showed that both purolite ion-exchange resins can remove nitrate and phosphate. But the removal of nitrate was higher (almost 80%) by Purolite A520E than by Purolite A500PS (65%) (Fig. 1(a)). It could be due to the fact that Purolite A520E is reported to be a nitrate-selective resin that can remove higher amounts of nitrate than Purolite A500PS which is usually recommended for organic removal [31]. In contrast to nitrate removal, Purolite A500PS showed a higher removal efficiency of phosphate (almost 65%) than Purolite A520E (48%)

Table 2  
The equations for the adsorption isotherms and kinetic models

Models	Equation	Linearized form
Langmuir isotherm	$Q_e = \frac{q_{\max}K_L C_e}{1 + K_L C_e}$ <p><math>C_e</math> = the equilibrium concentration of the adsorbate (mg/L);  <math>Q_e</math> = the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g); <math>q_{\max}</math> = the maximum amount of the adsorbate per unit weight of the adsorbent (mg/g); <math>K_L</math> = Langmuir constant (L/mg)</p>	$\frac{C_e}{Q_e} = \frac{1}{q_{\max}K_L} + \frac{C_e}{q_{\max}}$
Freundlich isotherm	$q_e = K_F C_e^{1/n}$ <p><math>C_e</math> = the equilibrium concentration of the adsorbate (mg/L);  <math>q_e</math> = the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g); <math>K_F</math> and <math>n</math> = Freundlich constants (mg/g)</p>	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$
Pseudo-first-order kinetic	$\frac{dq_t}{dt} = k_1(q_e - q_t)$ <p><math>q_e</math> = amount of nutrients adsorbed at equilibrium (mg/g);  <math>q_t</math> = amount of nutrients adsorbed at time, <math>t</math> (min) (mg/g); and  <math>k_1</math> = equilibrium rate constant of pseudo-first-order sorption (1/min).</p>	$\ln(q_e - q_t) = \ln q_e - k_1 t$
Pseudo-second-order kinetic	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$ <p><math>q_e</math> = amount of nutrients adsorbed at equilibrium (mg/g);  <math>q_t</math> = amount of nutrients adsorbed at time, <math>t</math> (min) (mg/g); and  <math>k_2</math> = equilibrium rate constant of pseudo-second-order (1/min).</p>	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$

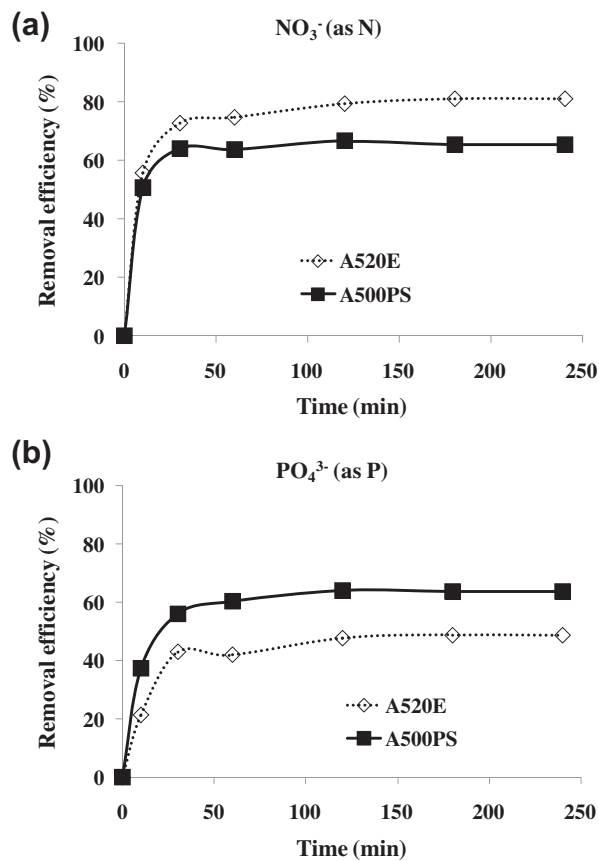


Fig. 1. Comparison between two purolite ion-exchange resins in removing (a) nitrate and (b) phosphate (initial concentration of nitrate and phosphate was  $20 \text{ mg NO}_3^-/\text{L}$  (as N) and  $10 \text{ mg PO}_4^{3-}/\text{L}$  (as P) respectively, dose of ion-exchange resin =  $1.5 \text{ g/L}$ ).

(Fig. 1(b)). Similar findings were also observed by Johir et al. [30] in column adsorption experiments of nitrate and phosphate from MBR effluents containing  $\text{PO}_4^{3-}$ -P and  $\text{NO}_3^-$ -N concentrations of  $3.1$  and  $11 \text{ mg/L}$ , respectively, by Purolite A520E and Purolite A500PS (previously known as A500P). They found that the removal of nitrate was almost 94% by Purolite A520E and the removal of phosphate was only 25–45%. The removal efficiency of phosphate was observed to be higher for Purolite A500P than for Purolite A520E. However, the removal efficiency of nitrate by the two resins was almost the same. The results in Fig. 1 as well as those of Johir et al. [30] show that A520E has a strong selectivity for  $\text{NO}_3^-$  than for  $\text{PO}_4^{3-}$  but A500P appear to have nearly the same affinity for  $\text{PO}_4^{3-}$  as  $\text{NO}_3^-$  when the influent N/P concentration ratio was 2:1.

A second set of experiments was conducted to study the effect of the presence of phosphate on the removal of nitrate by the two purolites (Fig. 2(a) and

(c)) and the effect of the presence of nitrate on the removal of phosphate by the two purolites (Fig. 2(b) and (d)) at two concentrations of P and N. Fig. 2(a) shows that the removal of nitrate by Purolite A520E was not affected by the presence of phosphate. However, the removal efficiency of phosphate by Purolite A520E in the presence of nitrate decreased by almost 50% (Fig. 2(b)). It may be due to the lower affinity of Purolite A520E towards phosphate ion than towards nitrate ion during ion-exchange processes as Purolite A520E is a highly nitrate-selective resin. These results show that in the presence of nitrate and phosphate in water, nitrate can effectively compete with phosphate for adsorption on Purolite A520E.

The removal efficiency of nitrate and phosphate by Purolite A500PS is similar to Purolite A520E. The removal efficiency of phosphate by Purolite A500PS decreased from 80–86% to less than 60% in the presence of low concentration of nitrate, and in the case of high concentration of nitrate, it decreased from 82 to 34% (Fig. 2(c)). It is also found that the removal efficiency of nitrate by Purolite A500PS was not very much affected by the presence of phosphate, and in the case of high concentration of phosphate, it slightly decreased. This shows that nitrate is effectively competing with phosphate in Purolite A500PS as well. Although Purolite A500PS can remove both nitrate and phosphate effectively, it is also a nitrate-selective resin.

The above experiments were conducted at two ratios and two concentrations of nitrate and phosphate. To evaluate further the influence of the competitive effects of nitrate and phosphate on their removals by these two purolite ion-exchange resins and to determine the selectivity of the resins for nitrate and phosphate, further experiments were conducted at more than two concentrations and two ratios of nitrate and phosphate. The results are presented in Fig. 3(a) and (b). It was found that at different ratios of N to P (1:1–1:5) (concentration of nitrate increased), the ratio of the amounts of N to P adsorbed was higher than the ratio of the initial solution concentrations of N to P for both purolites (Fig. 3(a)). This shows that both purolites are nitrate selective. At all N-to-P ratio in solution, the ratio of N to P adsorbed was higher for Purolite A520E than for Purolite A500PS, which suggests that the nitrate selectivity for adsorption was higher for Purolite A520E than for Purolite A500PS. The selectivity of Purolite A520E for nitrate increased at a faster rate than that of Purolite A500PS with increase in N/P ratio. When the P/N ratio in solution was increased at a constant concentration of nitrate ( $\text{N} = 50 \text{ mg/L}$ ) (Fig. 3(b)), the P/N ratio of adsorbed nutrients was increased as expected

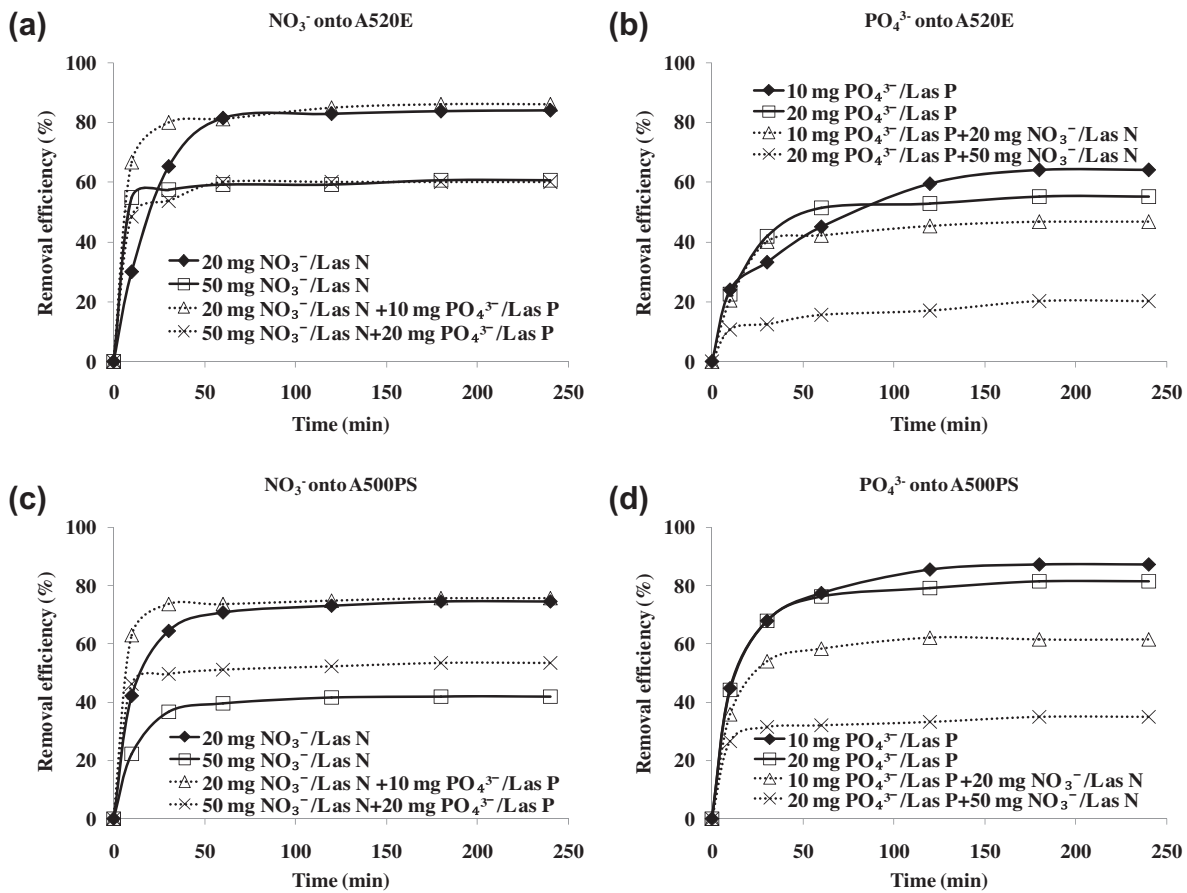


Fig. 2. Effect of the presence of phosphate and nitrate on the removal of nitrate and phosphate (a, b) by Purolite A520E and (c, d) by Purolite A500PS (dose of ion-exchange resin = 1.5 g/L).

but this ratio in the resin was lower than in solution, showing that both resins are nitrate selective as observed in Fig. 3(a). However, the P/N ratio in resin was higher for Purolite A500PS than for Purolite A520E, showing that the nitrate selectivity for adsorption is lower for A500PS as again observed in Fig. 3 (a).

### 3.2. Modelling of adsorption isotherm

In general, the results of the equilibrium adsorption isotherm experiments showed an increase in removal efficiency of nitrate and phosphate with an increase in ion-exchange resin concentrations onto Purolite A520E and Purolite A500PS. It could be due to the reasons that (i) maximum adsorption capacity of the resins has not reached and (ii) solution concentration of adsorbate has been reduced to very low concentration.

The equilibrium adsorption data were fitted to Langmuir and Freundlich isotherm models. Both

models fitted well for the adsorption of nitrate on Purolite A520E ( $R^2=0.95-0.96$ ) (Table 3). However, the adsorption of nitrate on Purolite A500PS can be explained satisfactorily only by Freundlich model, which showed a good correlation ( $R^2=0.983$ ). The data fit to Langmuir model was very poor ( $R^2=0.033$ ).

On the other hand, the data for the adsorption of phosphate on both resins did not fit well to Langmuir model (Table 3). However, the adsorption of phosphate on the resins fitted well to Freundlich model, which showed a high coefficient of determination ( $R^2=0.901$ ) for Purolite A500PS as well as for Purolite A520E ( $R^2=0.897$ ). The model parameters ( $K_L$ ,  $q_{max}$ ,  $K_F$  and  $n$ ) obtained from the simulations are presented in Table 3. The maximum value of nitrate adsorption on Purolite A520E was found to be 33 mg N/g using Langmuir equation, and the Freundlich parameter  $K_F$  was 4.29 (mg N/g)(L/mg N)<sup>1/n</sup>. Samatya et al. [22] reported that the maximum adsorption capacity of nitrate on Purolite A520E was 18.51 mg N/g from Langmuir fit and the Freundlich parameter  $K_F$  was

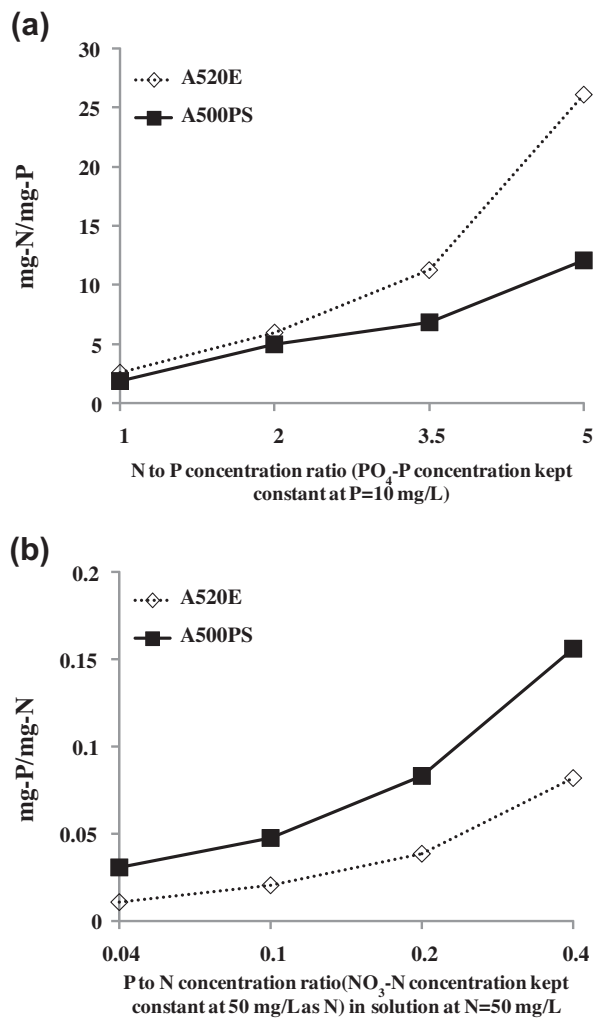


Fig. 3. Effect of solution (a) N-to-P ratio and (b) P-to-N ratio on the N/P and P/N removal by purolite resins, respectively.

$3.33(\text{mg N/g})(\text{L}/\text{mg N})^{1/n}$  in batch experiment. Primo et al. [24] reported that the maximum adsorption

capacity of nitrate on purolite from a column experiment was  $18.81 \text{ mg N/g}$ . According to the manufacturer's information, A520E resin has quaternary ammonium as a functional group, with a total ion-exchange capacity of  $2.8 \text{ meq/g}$  of dry resin ( $39.2 \text{ mg N/g}$ ) (Table 1). The Langmuir maximum adsorption capacity obtained in the current study ( $33 \text{ mg N/g}$ ) agrees fairly well with the manufacturer value. The maximum phosphate adsorption capacity on Purolite A500PS was found to be  $111.11 \text{ mg P/g}$  from Langmuir equation, and the Freundlich parameter  $K_F$  was  $4.49(\text{mg P/g})(\text{L}/\text{mg P})^{1/n}$ .

### 3.3. Modelling of adsorption kinetics

In adsorption kinetics, mass transfer and diffusion of adsorbate particles from bulk liquid phase to adsorbent surface determine the rate of adsorption. The adsorption data showed that generally pseudo-first-order kinetic model had poor fit to the data for the adsorption of nitrate and phosphate on both purolites (Tables 4 and 5). Only for the lower resin dose of  $1.5 \text{ g/L}$ , the data fitted satisfactorily to pseudo-first-order kinetic model for both nitrate and phosphate adsorption on both resins.

In contrast to the pseudo-first-order kinetic model, the adsorption of phosphate and nitrate onto both ion-exchange resins was much better evaluated by pseudo-second-order kinetic model with  $R^2$  of 0.99 and above (Tables 4 and 5). Previous studies of nitrate adsorption on purolite also showed that the kinetics adsorption data were better described by pseudo-second-order kinetic model [23].

Furthermore, the values of  $q_e$  calculated from pseudo-first-order kinetic model were lower than the experimental value of  $q_{e,r}$ , while the experimental values of  $q_e$  were almost similar to the  $q_e$  values calculated from the pseudo-second-order kinetic model

Table 3

Adsorption isotherm parameters of Langmuir and Freundlich models for nitrate and phosphate adsorption on Purolite A520E and Purolite A500PS

	Adsorption of nitrate onto		Adsorption of phosphate onto	
	Purolite A520E	Purolite A500PS	Purolite A520E	Purolite A500PS
<i>Langmuir isotherm model</i>				
$q_{\text{max}}$ (mg N,P/g)	33	1,000	–250	111
$K_L$ (L/mg)	0.143	0.003	–0.012	0.055
$R^2$	0.961	0.033	0.016	0.574
<i>Freundlich Isotherm Model</i>				
$K_F$ (mg N,P/g)(L/mg N,P) <sup>1/n</sup>	4.29	2.45	3.40	4.49
$n$	1.54	1.03	1.12	0.909
$R^2$	0.953	0.983	0.897	0.901

Table 4

Adsorption kinetic parameters of pseudo-first-order and pseudo-second-order kinetics models for the adsorption of nitrate onto Purolite A520E and Purolite A500PS

Purolite	Concentration of purolite (mg/L)	Concentration of raw water (mg N/L)	$q_e$ experimental (mg N/g)	Pseudo-first-order model			Pseudo-second-order model		
				$q_e$ (mg N/g)	$k_1 \times 10^{-2}$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ (mg N/g)	$k_2 \times 10^{-2}$ (g/mg min)	$R^2$
A520E	1.5	20	11.00	3.38	1.76	0.82	11.60	0.71	0.99
		50	19.30	1.86	14.4	0.91	19.34	2.62	0.99
	3.0	20	5.70	0.46	0.81	0.48	5.66	9.31	0.99
		50	12.60	1.23	1.32	0.88	12.62	4.00	1.0
A500PS	1.5	20	10.97	3.19	2.08	0.94	11.36	1.37	0.99
		50	14.95	3.93	2.82	0.91	15.63	0.85	0.99
	3.0	20	4.91	0.42	0.76	0.39	4.97	9.86	0.99
		50	9.25	1.17	1.26	0.85	8.35	2.47	0.99

Table 5

Adsorption kinetic parameters of pseudo-first-order and pseudo-second-order kinetics models for the adsorption of phosphate onto Purolite A520E and Purolite A500PS

Purolite	Concentration of purolite (mg/L)	Concentration of raw water (mg P/L)	$q_e$ experimental (mg/g)	Pseudo-first-order			Pseudo-second-order		
				$q_e$ (mg/g)	$k_1 \times 10^{-2}$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ (mg/g)	$k_2 \times 10^{-2}$ (g/mg min)	$R^2$
A520E	1.5	10	5.06	6.69	3.1	0.93	5.85	0.51	0.99
		20	8.2	6.68	3.5	0.91	8.70	0.92	0.99
	3.0	10	1.95	0.38	1.85	0.84	2.25	4.34	0.99
		20	2.87	0.56	0.86	0.33	3.94	3.52	0.99
A500PS	1.5	10	7.10	6.58	4.11	0.93	7.45	1.32	0.99
		20	11.70	4.76	2.29	0.91	12.08	1.02	0.99
	3.0	10	3.60	0.49	1.79	0.82	3.65	8.51	0.99
		20	6.40	0.60	0.77	0.25	6.33	5.69	0.99

(Tables 4 and 5). These findings also demonstrated that the adsorption reaction can be satisfactorily described by the pseudo-second-order kinetic model. The satisfactory fits of the data to the second-order-kinetic models imply that the rates of ion-exchange process are limited only by the availability of nitrate and phosphate ions and functional groups from resin surface to interact [23].

#### 4. Conclusions

The ion-exchange resins, Purolite A520E and Purolite A500PS, can be used for the effective removal of nitrate and phosphate from water. Both purolites preferentially removed nitrate over phosphate from solutions containing these two ions at various concentration ratios, and hence, they are considered to be

nitrate selective. The nitrate selectivity for adsorption was higher for Purolite A520E than for Purolite A500PS. Purolite A500PS is more efficient in removing phosphate than Purolite A520E. The adsorption of phosphate and nitrate on both purolites was much better described by pseudo-second-order kinetic model than by pseudo-first-order kinetic model. Freundlich model was better fitted for the adsorption isotherm of nitrate and phosphate than Langmuir model on both purolites.

#### Acknowledgment

This work was funded by Australian Research Council Discovery Research Grant (DP 1092603). Thanks to Vitachem for supplying purolites.



## References

- [1] S.E. Jorgensen, W.D. Williams, *Water Quality: The Impact of Eutrophication*, United Nations Environment, Program, 2001.
- [2] S.N. Levine, D.W. Schindler, Phosphorus, nitrogen and carbon dynamics of experimental Lake 303 during recovery from eutrophication, *Can. J. Fish. Aquat. Sci.* 46 (1989) 2–10.
- [3] A.P. Murphy, Chemical removal of nitrate from water, *Nature* 350 (1991) 223–225.
- [4] World Health Organization (WHO). *Guidelines for Drinking-water Quality*, 2006. Available from: [http://www.who.int/water\\_sanitation\\_health/dwq/gdwq0506.pdf](http://www.who.int/water_sanitation_health/dwq/gdwq0506.pdf).
- [5] D.A. Clifford, X. Liu, J. Am, Biological denitrification of spent regenerant brine using a sequencing batch reactor, *Water Res.* 9 (1993) 1477–1484.
- [6] B. Bae, Y. Jung, W. Han, H. Shin, Improved brine recycling during nitrate removal using ion exchange, *Water Res.* 36 (2002) 3330–3340.
- [7] M. Boumediene, D. Achour, Denitrification of the underground waters by specific resin exchange of ion, *Desalination* 168 (2004) 187–194.
- [8] N. Lohumi, S. Goasin, A. Jain, V.K. Gupta, K.K. Verma, Determination of nitrate in environmental water samples by conversion into nitrophenols and solid phase extraction–spectrophotometry, liquid chromatography or gas chromatography mass spectrometry, *Analytica Chimica Acta* 505 (2004) 231–237.
- [9] H. Mori, Characterization of a potential catalytic residue, Asp-133, in the high affinity ATP-binding site of *Escherichia coli* SecA, Translocation ATPase, *J. Biol. Chem.* 271 (1996) 17439–17444.
- [10] E. Wasik, J. Bohdziewicz, M. Blasszezyk, Removal of nitrates from ground water by a hybrid process of biological denitrification and microfiltration membrane, *Process Biochem.* 37 (2001) 57–64.
- [11] K. Lüdtke, K. Peinermann, V. Kasche, R. Behling, Nitrate removal of drinking water by means of catalytically active membranes, *J. Membr. Sci.* 151 (1998) 3–11.
- [12] R. Gavagnin, L. Biasetto, F. Pinna, G. Strukul, Nitrate removal in drinking waters: The effect of tin oxides in the catalytic hydrogenation of nitrate by Pd/SnO<sub>2</sub> catalysts, *Appl. Catal. B: Environ.* 38 (2002) 91–99.
- [13] J.J. Schoeman, A. Steyn, Nitrate removal with reverse osmosis in a rural area in South Africa, *Desalination* 155 (2003) 15–26.
- [14] F. Hell, J. Lahnsteiner, H. Frischherz, G. Baumgartner, Experience with full-scale electro dialysis for nitrate and hardness removal, *Desalination* 117 (1998) 173–180.
- [15] A. Elmidaoui, F. Elhannouni, Optimization of nitrate removal operation from ground water by electro dialysis, *Sep. Purif. Technol.* 29 (2002) 235–244.
- [16] J.W. Peel, K.J. Reddy, B.P. Sullivan, J.M. Bowen, Electrocatalytic reduction of nitrate in water, *Water Res.* 37 (2003) 2512–2519.
- [17] D.Y. Zhao, A.K. Sengupta, Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers, *Water Res.* 32 (1998) 1613–1625.
- [18] Z.H. Li, R. S Bowman, Retention of inorganic oxyanions by organo-kaolinite, *Water Res.* 35 (2001) 3771–3776.
- [19] N.M. Agyei, C.A. Strydom, J.H. Potgieter, The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary Portland cement and related blends, *Cement Concrete Res.* 32 (2002) 1889–1897.
- [20] U.S. Orlando, A.U. Baes, W. Nishijima, M. Okada, Preparation of agricultural residue anion exchangers and its nitrate maximum adsorption capacity, *Chemosphere* 48 (2002) 1041–1046.
- [21] M. Ozacar, Adsorption of phosphate from aqueous solution onto alunite, *Chemosphere* 51 (2003) 321–327.
- [22] S. Samatya, N. Kabay, U. Yuksel, M. Arda, M. Yuksel, Removal of nitrate from aqueous solution by nitrate selective ion-exchange resins, *React. Funct. Polym.* 66 (2006) 1206–1214.
- [23] L. Bulgariu, A. Ceica, L. Lazar, I. Cretescu, I. Balasanian, Equilibrium and kinetics study of nitrate removal from water by Purolite A100 resin, *Rev. Chim.* 61 (2010) 1136–1141.
- [24] O. Primo, M. Rivero, A. Urtiaga, I. Ortiz, Nitrate removal from electro-oxidized landfill leachate by ion exchange, *J. Hazard. Mater.* 164 (2009) 389–393.
- [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, O. Kim, D.L. Hardan, Nitrate removal from contaminated ground water, *Amer. Water Works Assoc.* 91 (1999) 79–91.
- [27] P.A. Terry, Removal of nitrates and phosphates by ion exchange with hydrotalcite, *Environ. Eng. Sci.* 26 (2009) 691–696.
- [28] L. Lv, P. Sun, Y. Wang, H. Du, T. Gu, Phosphate removal and recovery with calcined layer double hydroxides as an adsorbent, *Phosphorus Sulfur Silicon* 183 (2008) 519–526.
- [29] S. Burge, R. Halden, Report on Environmental Restoration Division, Lawrence Livermore National Laboratory, UCRL-ID-135639, University of California, Livermore, CA, 1999.
- [30] 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.
- [31] [www.purolite.com](http://www.purolite.com)-Purolite A520E, Technical data, ISO 9002.