

## **Removing ammonium from contaminated water using Purolite C100E: Batch, column, and household filter studies**

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### **ABSTRACT**

Ammonium removal from drinking water to protect human and environmental health is one of the major global concerns. This study evaluates the performance of Purolite C100E, a commercial cation exchange resin, in eliminating ammonium in synthetic and real contaminated groundwater. The results demonstrate that the pH operation range of the resin for better ammonium removal is 3 to 8. Lower ammonium removal at low and high pH occurred due to competition from H<sup>+</sup> and loss of ammonium as ammonia gas, respectively. Equilibrium data of ammonium removal fitted both the Langmuir and Freundlich isotherm models with the maximum Langmuir ion exchange capacities for initial ammonium concentrations of 10-200 mg/L and 50-2000 mg/L, reaching 18.37 mg/g and 40.16 mg/g, respectively. The presence of co-ions in the water reduced the ammonium removal efficiencies slightly (<12%) in the order Mg<sup>2+</sup>> Ca<sup>2+</sup>> K<sup>+</sup>. The higher affinity of ammonium to adsorbent is due to its lower hydrated ionic radius and H-bonding. The maximum exchange capacity in the fluidized bed studies of the original Purolite C100E (bed height 27 cm, resin weight 75 g, initial ammonium concentration 17.4 mg/L, filtration velocity 0.5 m/h) was 10.48 mg/g. It progressively reduced slightly after three regeneration cycles to 8.79 mg/g. The column breakthrough data satisfactorily fitted the Thomas model. A household filter cartridge packed with 4 kg Purolite C100E (80 cm height) and operated at a filtration velocity of

1.9 m/h in Vietnam successfully reduced the initial 6 mg NH<sub>4</sub><sup>+</sup>/L in groundwater (after sand filter pre-treatment) to well below the Vietnam drinking water standard (3 mg/L-QCVN 01:2009/BYT) continuously for one week, suggesting that such a filter can be adopted in rural areas to successfully remove ammonium from groundwater.

**Keywords:** Ammonium removal; Contaminated water; Ion exchange; Household water filter; Purolite C100-E resin

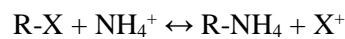
## 1. Introduction

One of the most serious global problems currently facing humanity is the inability to provide clean water for drinking and other purposes. The lack of clean water is threatening the lives of billions of people in many countries around the world, especially in developing countries ([Aliewi and Al-Khatib, 2015](#); [Tanabe et al., 2001](#); [Sica et al., 2014](#)). Vietnam, a country in Southeast Asia, is no exception.

In Vietnam, clean water for drinking and living needs is provided from surface water (rivers, lakes, and streams), rainwater, and groundwater. In many rural areas, groundwater is the main water source for human sustenance and daily activities. Groundwater is often exploited through dug wells or drilled wells, and pre-treated by filtering through sand filter tanks prior to use in households ([Terin and Sabogal-Paz, 2019](#)). The quality of groundwater in each locality fluctuates very widely and is unstable, depending on many factors, including groundwater circuits, geological conditions, and human activities. The groundwater treated by a conventional sand filter normally still contains many pollutants such as arsenic, iron, manganese, and ammonium, exceeding the permitted standard concentration limits. Among these pollutants, ammonium is considered one of the most common and difficult pollutants to eliminate ([Vu et al., 2017](#); [Alshameri et al., 2014](#)). In Hanoi (Vietnam), groundwater with high ammonium concentrations of 55-70 mg/L was reported in some villages ([Vietnam Environment Agency, 2016](#)). In another study conducted in three villages in Ha Nam Province of Vietnam, average groundwater ammonium concentrations of 22-95 mg/L were detected in 2006, with some samples having values greater than 150 mg/L ([Nguyen et al., 2009](#)). These values were 7 to 32 times higher than the Vietnam drinking water standard (3 mg/L, [Vietnamese Department of Preventive Medicine & Environment,](#)

[2009](#)). Not only Vietnam but there are many other countries that have similar excessive levels of ammonium pollution in their groundwater sources. Examples include Dongting Plain, central China ([Huang et al., 2021](#)), Bangladesh ([Tanabe et al., 2001](#)), Palestine ([Aliewi and Al-Khatib, 2015](#)), and Montana in the USA ([Shaw et al., 2013](#)). Ammonium in groundwater mainly derives from human and waste contamination ([Rusydi et al., 2021](#)) or buried peat layers in the soil ([Norrman et al., 2015](#)). Due to its toxicity to human health, ammonium in groundwater should be removed, and this is one of the major challenges the water treatment industry is currently facing.

There are several technologies that can remove ammonium from water, such as biological nitrification/denitrification, air stripping, chlorination, adsorption, ion exchange, and membrane processes ([Sica et al., 2014](#); [Ding and Sartaj, 2016](#); [Aral et al., 1999](#)). Of these, ion exchange is known to be one of the most widely applied technologies in removing ammonium ([Tchobanoglous et al., 2014](#)). In this process, specific ions in the solution displace ions of a similar charge from an exchange material. The main principle of this approach can be summarised for ammonium exchange on ion exchange resin employing the following equation:



where R<sup>-</sup> is the anionic group of an ion exchange resin and X is the exchangeable cation neutralizing the anionic charge.

Ion exchangers can be classified as natural materials (natural zeolite) and synthetic organic resins ([Ding and Sartaj, 2016](#)). Compared with natural zeolite, synthetic resins have many advantages, such as: longer life cycle, faster exchange rate, better durability, and higher exchange capacity ([Ding and Sartaj, 2016](#); [Aral et al., 1999](#)). In groundwater, there are many co-existing ions such as calcium and magnesium present along with ammonium, and these ions can compete with ammonium for ion exchange. Such competition will reduce efficiency in removing ammonium via an ion exchanger. Only a few studies reported in the literature have evaluated the treatment efficiency of ammonium ions in not only water sources generally but also real groundwater, in particular by ion exchange resins. [Jorgensen and Weatherley \(2003\)](#) reported that Dowex 50W-X8 and Purolite MN500 ion exchange resins had maximum exchange capacity of approximately 35 and 29 mg/g, respectively, at the initial concentration of 200 mg NH<sub>4</sub><sup>+</sup>/L synthetic solution. [Ding and Sartaj \(2016\)](#) reported that Amberlite IR120 H resin had

a Langmuir maximum exchange capacity of 29.76 mg/L at an initial concentration of 300-3000 mg  $\text{NH}_4^+$ /L synthetic solution.

One of the most popular ion exchange resins used for water treatment in Vietnam is Purolite C100-E resin (Purolite Co., UK). This resin is already in use not only in Vietnam but also in many other countries for reducing the hardness of domestic water sources. To the best of the authors' knowledge, no study has yet evaluated this resin for the treatment of ammonium in water. Therefore, this study was undertaken to evaluate the additional advantage of Purolite C100-E ion exchange resin for ammonium removal from groundwater. If the resin is found to be effective in removing ammonium, it can then serve two purposes, namely, removing ammonium as well as water hardness, providing an additional advantage for the water treatment plants. Another aspect of the study was the evaluation of continuous ammonium removal by the resin in a dynamic column set-up, which can be applied to design practical groundwater treatment systems in rural areas. The regeneration efficiency of the resin was also studied to obtain information on the reusability of the resin, which would reduce the treatment cost. Finally, the study was conducted in the field with real contaminated groundwater containing competing cations at Ha Noi, Vietnam, in an effort to fully evaluate the practical performance of Purolite C100E. The studies in dynamic columns with mathematical modeling of ammonium breakthrough and field testing of the resin performance in household conditions are innovations researched in this paper.

## **2. Materials and methods**

### ***2.1. Ion exchange resin***

The ion exchange resin used in this study was Purolite C100-E (obtained from Purolite Co.). Purolite C100-E is a strong acid cation resin and structure-wise, it consists of gel polystyrene cross-linked with divinylbenzene ([Purolite Co, 2013](#)). The functional group of this resin is sulfonic acid ( $-\text{SO}_3\text{H}$ ), which contains the exchangeable ion  $\text{Na}^+$ . Purolite C100-E has a total exchange capacity of 1.90 eq/L ( $\text{Na}^+$  form), moisture retention of 46-50%, particle size from 300 to 1200  $\mu\text{m}$ , and density of 800 – 840 g/L. The resin was initially washed with distilled water to remove any dirt present in it. It was then dried at room temperature ( $30 \pm 1^\circ\text{C}$ ) for 24 h to remove adsorbed moisture.

## **2.2. Synthetic ammonium solution**

Ammonium stock solution of 2000 mg NH<sub>4</sub><sup>+</sup>/L was prepared by dissolving 11.888 g analytical-grade NH<sub>4</sub>Cl (Merk Chemical Co.) in 2000 mL distilled water. Then, the stock solution was diluted with distilled water to achieve the desired ammonium concentrations (20 to 2000 mg/L) for use in batch and column experiments.

## **2.3. Analytical methods**

The concentration of ammonium in the liquid phase was determined using a manual spectrometric method ([ISO 7150/1, 1984](#)). Here, the blue compound formed by the reaction of ammonium in solution with salicylate and hypochlorite ions in the presence of sodium nitrosopentacyanoferrate (III) was measured by a UV-VIS spectrophotometer (Model 8453, Agilent Technologies, Inc., California, United States) at a wavelength of 655 nm (Detection limit = 0.008 mg/L).

Scanning electron microscopy (SEM, Model JSM-7500F, JEOL Ltd., Japan) served to investigate the surface morphology of the Purolite C100E resin particles before and after the ion exchange process. Meanwhile, the surface chemical elemental composition before and after the ion exchange process was determined by Energy Dispersion Spectrometry analysis (EDS, Model X-max 50 mm<sup>2</sup>, Oxford Instruments Analytical Ltd., England).

## **2.4. Batch studies**

Several batch ion-exchange experiments were conducted at room temperature of 30 ± 1°C to evaluate the performance of Purolite C100E for removing ammonium.

### **2.4.1. Effect of pH**

The effect of pH on ammonium removal by Purolite C-100E was studied at a range of pH values from approximately 1 to 11. Here the pH of synthetic ammonium solution of 50 mg/L was adjusted using HCl and NaOH standard solutions to achieve the desired pH values. As the pH changed from 1 to 11, the ionic strength also changed. To keep the ionic strength constant as much as possible for the pH levels, this experiment was repeated by adding NaCl to maintain the solutions at two ionic strengths:

0.001M and 0.01M NaCl. NaCl is an indifferent electrolyte, one that plays the role of a supporting medium to keep ionic strength constant throughout all pH level values ([Hedström and Amofah, 2008](#)). The experiments were conducted by adding 1.0 g resin to 100 mL synthetic ammonium solution containing 50 mg NH<sub>4</sub><sup>+</sup>/L at different levels of pH in several 250 mL Erlenmeyer flasks. These flasks were agitated at 130 rpm for 24 h. The suspensions were filtered through 0.45 µm filter papers, and the concentrations of ammonium in the filtrates were measured as explained before.

#### ***2.4.2. Kinetics experiment***

1.0 g resin was added to 100 mL synthetic ammonium solution containing 50 mg NH<sub>4</sub><sup>+</sup>/L in several 250 mL Erlenmeyer flasks. These flasks were agitated at 130 rpm, and samples were collected after 0, 5, 10, 15, 30, 45, 60, 90, 120, 180, and 240 min from each flask. The samples were filtered through 0.45 µm filter paper, and the concentrations of ammonium in the filtered samples were measured.

#### ***2.4.3. Equilibrium isotherm experiment***

##### *Effect of resin dose*

Synthetic water containing 50 mg NH<sub>4</sub><sup>+</sup>/L at pH 6.5 was used in this study. Different amounts of Purolite C100-E were added to 100 mL of the synthetic ammonium solution in a set of 250 mL Erlenmeyer flasks to produce concentrations from 0.5 to 20 g resin/L. The flasks were agitated in a shaker at 130 rpm for 24 h. The supernatants from the suspensions in these flasks were filtered through 0.45 µm filter papers and the concentrations of ammonium in the filtrates were measured.

##### *Isotherm experiment*

2.0 g resin was added to 100 mL synthetic ammonium solution to the different initial ammonium concentrations, ranging from 10 to 200 mg/L, in a set of 250 mL Erlenmeyer flasks. The flasks were agitated in a shaker at 130 rpm for 24 h. The supernatants from the suspensions in these flasks were then filtered through 0.45 µm filter paper, and the concentrations of ammonium in the filtrates were measured.

Another experiment was conducted using the same procedure, but the initial ammonium concentration ranged from 50 to 2000 mg/L to determine whether the maximum exchange capacity of

the resin calculated using standard adsorption models depends on the initial ammonium concentration range used.

The amount of ammonium in the solid phase was calculated using the mass balance [Equation 1](#) ([Wassie and Srivastava, 2016](#)):

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

where  $Q_e$  is the mass of ammonium exchanged per unit mass of resin (mg/g);  $C_o$  and  $C_e$  are specifically the initial and equilibrium concentrations of ammonium in the liquid phase (mg/L), respectively;  $V$  is the volume of solution (L) and  $m$  is the mass of Purolite C100-E resin (g).

The removal efficiency (RE, %) of ammonium was calculated using [Equation 2](#):

$$RE (\%) = \frac{(C_o - C_e)}{C_o} \cdot 100 (\%) \quad (2)$$

#### ***2.4.4. Effect of co-existing cations on ammonium removal***

Based on the [Vietnamese National Environmental Report \(2016\)](#), which covers the period 2011-2015, the groundwater in the northern delta region of Vietnam had Ca and Mg ions concentration ranging from 56.23-57.62 mg Ca<sup>2+</sup>/L and 34.71-36.98 mg Mg<sup>2+</sup>/L, respectively. Meanwhile, the K ion concentration in groundwater in the area ranged from 0.60 to 89 mg/L ([Nguyen et al., 2014](#)). An experiment was conducted by adding specifically potassium, calcium, and magnesium ions to the synthetic ammonium solution to determine the effects of these ions on ammonium removal by the resin. A fixed concentration of each cation (50 mg/L) was added to water containing five ammonium concentrations, ranging from 10 to 50 mg/L. The experimental procedure is similar to the equilibrium isotherm experiment.

#### ***2.5. Fluidised bed experiment***

A fluidised bed experiment was conducted using a glass column of 22 mm internal diameter and 300 mm height. The column was packed with 75 g Purolite C100E to have a height of 270 mm. For the long duration of 24 days of the column experiment, it was not able to obtain a sufficient volume of distilled water in the laboratory. Therefore, tap water was used instead in this experiment. Synthetic ammonium

solution ( $C_o \approx 17 \text{ mg NH}_4^+/\text{L}$ ) prepared from tap water was pumped upwards through the column by dosing pumps with a constant flow rate of 200 mL/h (corresponding to the filtration velocity of 0.5 m/h). The effluent samples were collected every 15 min for 238 h by an automatic sampling device, and the solutions were analyzed for ammonium (UV-VIS spectrophotometer, Model 8453, Agilent Technologies, Inc., California, USA) and other cations using an ICP-MS instrument (Model ELAN 9000, PerkinElmer, Inc., Shelton, USA).

The maximum amount of ammonium (mg) exchanged (removal) by the resin in the column was calculated using [Equation 3](#) (Kalaruban et al., 2016):

$$q_{total} = Q \cdot \int_{t=0}^{t-total} C_{ie} \cdot dt \quad (3)$$

where  $q_{total}$  is the maximum amount of ammonium exchanged by the resin (mg),  $Q$  is the flow rate of water (L/h),  $t$  is the operation time (h), and  $C_{ie}$  is the exchanged ammonium concentration ( $C_{ie} = C_o - C_t$ ) (mg/L).

The maximum ion exchange capacity of the resin ( $q_m$ , mg/g) was calculated from [Equation 4](#):

$$q_m = \frac{q_{total}}{M} \quad (4)$$

where  $M$  is the mass of resin used (g).

## 2.6. Fluidised bed column results modeling

The Thomas model ([Thomas, 1944](#)) was used to predict the breakthrough curve and the maximum ion exchange capacity of the material for ammonium in the fluidised bed column. This model assumes plug flow behaviour in the bed, uses the Langmuir isotherm for equilibrium and second-order reversible reaction for kinetics ([Nur et al., 2014](#)). The linearized form of the Thomas model can be expressed as follows ([Thomas, 1944](#)):

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_{Th}q_oM}{Q} - k_{Th}C_o t \quad (5)$$

where  $k_{Th}$  is the Thomas rate constant (mL/min mg);  $q_o$  is the maximum ammonium uptake per g of resin (mg  $\text{NH}_4^+/\text{g}$ );  $C_o$  is the inlet ammonium concentration (mg/L);  $C_t$  is the outlet ammonium concentration at time  $t$  (mg/L);  $M$  is the mass of resin (g);  $Q$  is the filtration rate (mL/min), and  $t$  stands for filtration time (min).



The Thomas rate constant  $k_{Th}$  and the ammonium exchange capacity of the bed  $q_o$  can be determined from a plot of  $\ln[(C_o/C)-1]$  against time (t).

### ***2.7. Regeneration of the resin used in the fluidised bed experiment***

Regeneration of the exhausted Purolite C100E after fluidised bed experiment was done by desorbing the adsorbed ammonium using 10% sodium chloride solution. Based on the [Purolite Engineering Bulletin document \(2013\)](#), this process was operated in counter-flow mode (up-flow mode), and it comprised of three steps as follows. Firstly, the regenerant brine was prepared by dissolving 100 g Indian industrial sodium chloride salt in 1L of distilled water to create a solution of 10% NaCl. This brine was pumped up-flow through the column at a rate of 2 BV/h (200 mL/h) for one hour. In the second step, a slow rinsing process was carried out using distilled water at the same flow rate as the first step for one hour. This removed the excess solution-phase sodium (unadsorbed) inside the resin. In the third step, a final rinse with distilled water was carried out at the experimental flow rate to achieve the same initial condition prior to the fluidised bed experiments. This process was conducted for about 20 minutes.

### ***2.8. Field trial at Hanoi, Vietnam***

A full-scale household filter cartridge was designed and used in an experiment with real contaminated groundwater at Hoang Mai district, Ha Noi, Vietnam, for the removal of ammonium. Before using the household filter cartridge, the real groundwater was pre-treated by a traditional sand filter tank to partly eliminate arsenic, iron, and ammonium. The effectiveness of sand filtration in the pre-treatment of contaminants in raw groundwater has been confirmed by various studies ([Sabogal-Paz et al., 2020](#); [Nitzsche et al., 2015](#)). The concentrations of contaminants in groundwater before and after the pre-treatment with the sand filter are shown in [Table 1](#). Although the sand filter removed a high percentage of all the contaminants, the ammonium concentration in the treated water was still above the maximum permitted concentration limit of Vietnam (3 mg/L). Therefore, the pre-treated water required further treatment, and the resin was used to investigate this.

**Table 1** - Contaminants in raw groundwater and after sand filtration

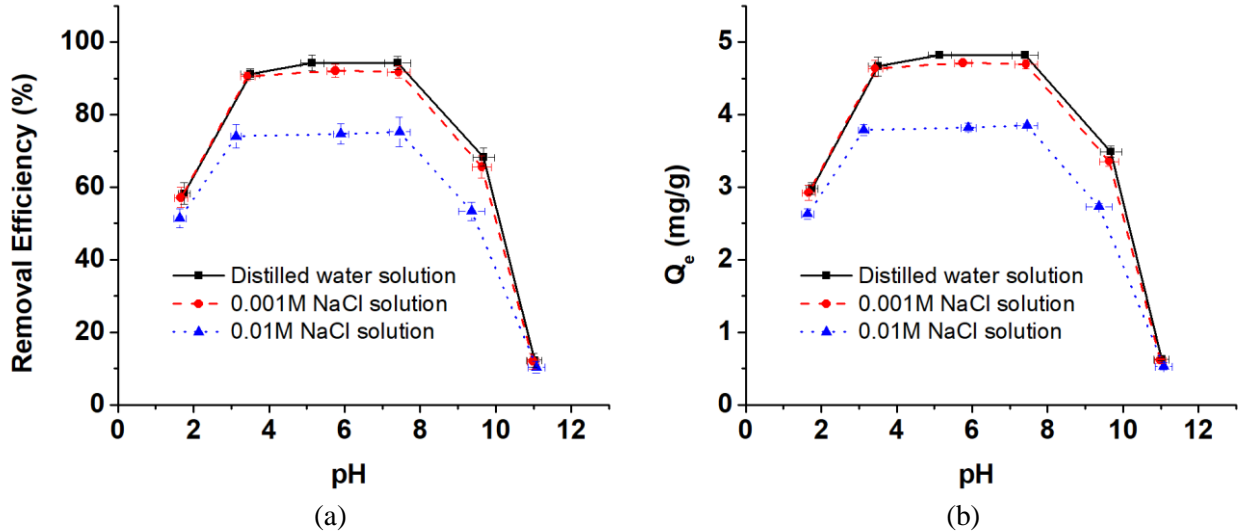
Contaminant	Raw groundwater	After sand filter
As ( $\mu\text{g/L}$ )	78.8	1.4
Fe ( $\text{mg/L}$ )	23	<0.05
$\text{NH}_4^+$ ( $\text{mg/L}$ )	25.73	5.92
Permanganate ( $\text{mg/L}$ )	1.72	1.29

The household filter cartridge used in this trial was fabricated from a PAC water pipe. It had an internal diameter of 10 cm containing 4 kg of Purolite C100E resin (corresponding to a bed height of about 80 cm). The pre-treated groundwater was pumped downward through the cartridge at a constant flow rate of 15 L/h (corresponding to a filtration velocity of 1.9 m/h). Water samples were collected every 12 h for one week and analyzed for ammonium, zinc, manganese, iron, calcium, magnesium, and sodium using an ICP-MS instrument (Model ELAN 9000, PerkinElmer, Inc., Shelton, USA).

### 3. Results and discussion

#### 3.1. Batch studies

##### 3.1.1. Effect of pH



**Fig. 1** - Effect of pH on (a) ammonium removal efficiency and (b) amount of ammonium removed (mg) per g resin ( $Q_e$ ) at three ionic strengths (Experimental conditions: resin dose = 10 g/L; initial  $\text{NH}_4^+$  concentration = 50 mg/L)

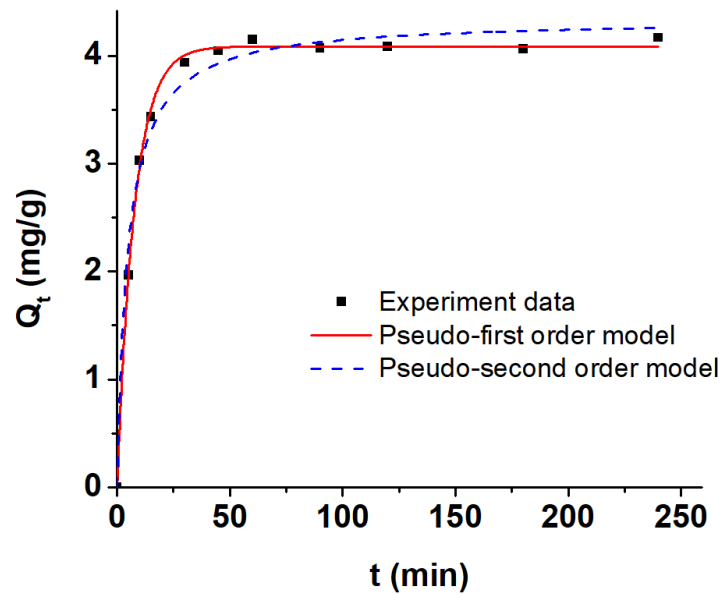
The data on the effect of pH on ammonium removal illustrated that the maximum removal efficiency occurred between pH 3 and 8 for all three ionic strength solutions (Fig. 1). When the pH was less than 3, the adsorption capacity was lower ( $< 4$  mg/g), which is explained by the competition between  $\text{H}^+$  in the highly acidic condition of the solution with  $\text{NH}_4^+$  ions for exchange (Vu et al., 2017).

The decline in ammonium removal efficiency was also observed when the pH was higher than 8. This is because at higher levels of pH,  $\text{NH}_4^+$  ions are converted to an un-ionized form ( $\text{NH}_3$ ) from having a reaction with the large amounts of  $\text{OH}^-$  ions generated when pH was increased by the addition of NaOH (Aral et al., 1999). Also, the Na added here would have competed with ammonium for cation exchange on the resin during these higher levels of pH, resulting in reduced ammonium removal. However, the reduction in ammonium removal occurred even in solutions having 0.01 M NaCl, where the Na concentration was nearly the same for any level of pH. This shows that Na competition with ammonium for exchange on the resin is not the major cause for the decline in ammonium removal at

higher levels of pH, but ammonium conversion to ammonia is the main reason for this. Based on these results, the initial pH value of the subsequent experiments was maintained at 6.5 to obtain larger amounts of ammonium being removed.

Compared with the distilled water solution containing  $\text{NH}_4^+$  (no addition of NaCl), the ammonium removal efficiency and the equilibrium exchange capacity ( $Q_e$ ) in the solution with 0.01M NaCl diminished considerably (Fig. 1). This is due to  $\text{Na}^+$  ions in the latter solution competing with  $\text{NH}_4^+$  ions for ion exchange in the resin (Aral et al., 1999). This competition is much less marked in the 0.001 M NaCl solution due to the smaller concentration of  $\text{Na}^+$  in this solution.

### 3.1.2. Effect of contact time and kinetics of exchange



**Fig. 2** - Pseudo-first order and Pseudo-second order model prediction of the kinetics of ammonium removal by the resin (Experimental conditions: resin dose = 10 g/L;  $\text{NH}_4^+$  initial concentration = 50 mg/L)

Fig. 2 shows that the rate of increase of  $Q_t$  with time in the first 20 min was very high and subsequently it reduced, and the exchange process reached equilibrium after 45 min. Sica et al. (2014) also reported a short time for the exchange of ammonium on Purolite C150H resin to reach equilibrium

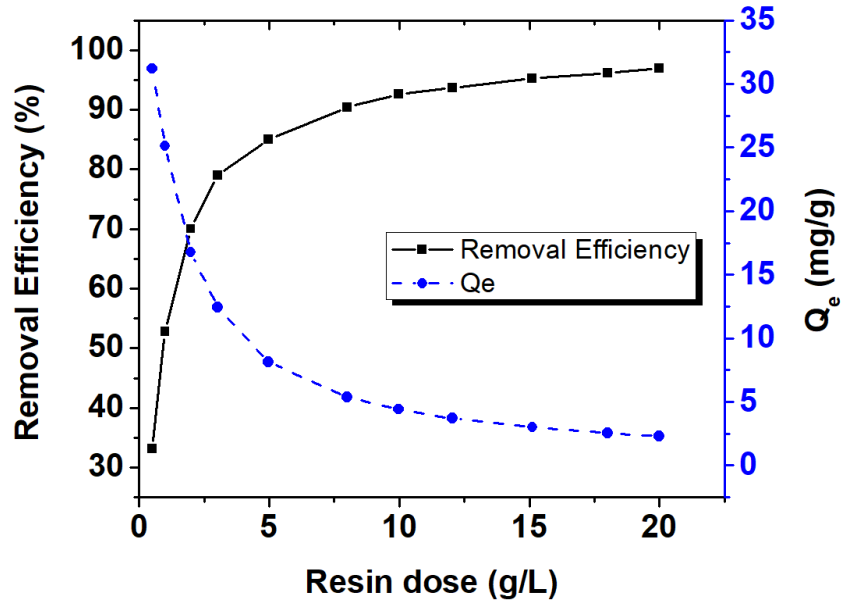
(40 min). Three common kinetic models were applied to describe the kinetics of ammonium removal by Purolite C100-E resin from the solution, namely, Elovich ([Li et al., 2009](#)), Pseudo-first order ([Tseng et al., 2009](#)), and Pseudo-second order ([Kumar and Sivanesan, 2006](#)). To determine the model that best fitted the data, non-linear regression analysis was applied. [Table 2](#) presents the non-linearised equations of the three kinetic models, their parameters and coefficient of determinations ( $R^2$ ) for the data fitting to the models.

**Table 2** - Kinetic models applied and parameters and coefficient of determinations ( $R^2$ ) obtained from the model fits to the data

Model	Non-linearised equation	$R^2$	Parameters	Equation description
Pseudo-first order	$q_t = q_e \cdot (1 - e^{-k_1 t})$	0.9983	$q_e = 4.08$ $k_1 = 0.1299$	$t$ is the contact time (min); $q_t$ is the amount of ammonia ion removed per g of resin at time $t$ (mg/g); $q_e$ is the $q_t$ value at equilibrium (mg/g); $k_1$ is the rate constant of pseudo-first order expression ( $\text{min}^{-1}$ )
Pseudo-second order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	0.9866	$q_e = 4.33$ $k_2 = 0.04907$	$k_2$ is the rate constant of pseudo-second order expression (g/mg min)
Elovich	$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$	0.9249	$\alpha = 24.01$ $\beta = 2.08$	$\alpha$ is the initial adsorption rate (mg/g min); $\beta$ is the desorption constant (g/mg)

As can be seen from [Table 2](#), both Pseudo-first order and Pseudo-second order models had higher  $R^2$  values (0.9983 and 0.9866, respectively) compared to the Elovich model ( $R^2 = 0.9249$ ). It means that these models can describe the kinetics of ammonium exchange. The comparison between experimental data and the data predicted from the two models is presented in [Fig. 2](#). [Khalil et al. \(2018\)](#) have reported that both models can be applied to describe ammonium exchange in Dowex HCR-S resin.

### 3.1.3. Effect of resin dose and equilibrium exchange isotherms



**Fig. 3** - Effect of resin dose on the removal efficiency of ammonium and amount exchanged ( $Q_e$ ) (Experimental conditions: resin doses: 0.2 - 20 g/L;  $\text{NH}_4^+$  initial concentration: 50 mg/L; 24 h shaking)

As can be seen from [Fig. 3](#), the removal efficiency of ammonium increased drastically when the resin dose rose, and beyond the resin dose of 10 g/L, the removal efficiency became almost constant at about 90%. The reason for the removal efficiency reaching a maximum of 90% and remaining almost constant is that nearly all ammonium in the solution was removed by the resin. Based on this result, a dose of 10 g/L was chosen as the optimum resin dose for the subsequent experiments.

Two common isotherm models (Langmuir and Freundlich) were implemented to evaluate the equilibrium ammonium adsorption properties of the resin. The mathematical equation of Langmuir isotherm ([Langmuir, 1918](#)) is given below ([Equation 6](#)):

$$Q_e = \frac{KbC_e}{1+KC_e} \quad (6)$$

where  $Q_e$  is the mass of ammonium exchanged onto solid phase per unit mass of resin at equilibrium (mg/g);  $K$  (L/mg) and  $b$  (mg/g) are Langmuir constants; and  $C_e$  is the equilibrium concentration of ammonium in solution (mg/L).

The Freundlich isotherm equation ([Freundlich, 1906](#)) is presented below ([Equation 7](#)):

$$Q_e = K_f C_e^{1/n} \quad (7)$$

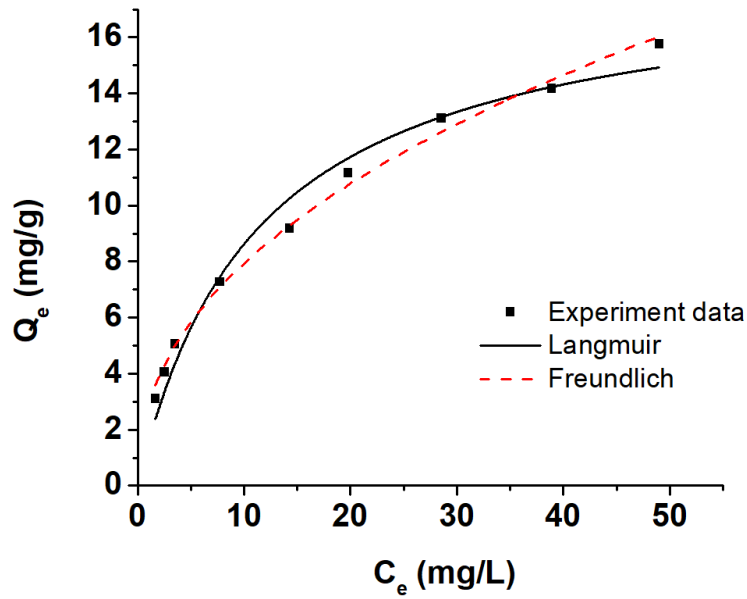
where  $Q_e$  is the mass of ammonium exchanged onto solid phase per unit mass of resin at equilibrium (mg/g);  $C_e$  is the equilibrium concentration of ammonium in solution (mg/L);  $K_f$  is Freundlich capacity factor ((mg/g) (L/mg)<sup>1/n</sup>); and  $1/n$  is Freundlich intensity parameter.

[Fig. 4](#) shows the prediction curves for the adsorption when Langmuir and Freundlich isotherm models were fitted to data compared to actual experimental data. As can be seen from [Table 3](#), both models fitted to the data very well with the Freundlich isotherm model providing a slightly better fit ( $R^2 = 0.9936$ ) compared to the Langmuir isotherm model ( $R^2 = 0.9752$ ). The maximum adsorption capacity ( $Q_{max}$ ) of the resin calculated from coefficient  $b$  in the Langmuir equation is 18.37 mg/g. This value is lower than the values reported by others for Amberlite IR120 H resin (29.76 mg/g) ([Ding and Sartaj, 2016](#)) and for Purolite MN500 (approximately 26 mg/g) and Dowex 50w-x8 (approximately 35 mg/g) ([Jorgensen and Weatherley, 2003](#)). This outcome is also slightly lower than those reported for few other materials ([Table 4](#)). The higher values obtained by others emerge because they used much higher solution concentrations of ammonium in their experiments (up to 3000 mg NH<sub>4</sub><sup>+</sup>/L) which are not relevant to field conditions ([Table 4](#)) compared to the concentrations used in the current experiment on Purolite C100E (10 to 200 mg NH<sub>4</sub><sup>+</sup>/L). In addition, the equilibrium time of Purolite MN500 and Dowex 50w-x8 ([Jorgensen and Weatherley, 2003](#)) was much higher (4 days) compared to the Purolite C100E resin in the current experiments (only 45 min). Using higher solution concentrations would give higher Langmuir maximum exchange capacity. This has been proved in the second adsorption experiment conducted where the initial ammonium concentrations were increased to a range of 50 to 2000 mg/L, and this increased the Langmuir maximum exchange capacity of Purolite C100E to 40.16 mg/g. This value is higher than that of Amberlite IR120 H resin (29.76 mg/g) ([Ding and Sartaj, 2016](#)) and Dowex 50w-x8 (35 mg/g) ([Jorgensen and Weatherley, 2003](#)) under the same test conditions (at high initial ammonium concentrations).

The favourable nature of ammonium adsorption on Purolite C100E was investigated from the  $K$  value of the Langmuir isotherm model ([Table 3](#)) using a dimensionless constant  $R_L$  according to the following equation:

$$R_L = \frac{1}{1+(1+K.C_0)} \quad (8)$$

where  $C_o$  is the maximum initial ammonium concentration. The calculated  $R_L$  values (from 0.05 to 0.2) lie between 0 and 1, indicating that the adsorption process is favourable ((unfavourable ( $R_L > 1$ ), favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ )) (Demir et al., 2008; Rusmin et al., 2015). The value of the Freundlich intensity parameter  $1/n$  (0.4433, Table 3) also lies between 0 and 1, indicating again a favourable adsorption process (Nguyen et al., 2020). It is consistent with the conclusion derived from the Langmuir model.



**Fig. 4** - Equilibrium data for ammonium removal using the resin fitted to the Langmuir and Freundlich isotherms

**Table 3** - Parameters of Langmuir and Freundlich isotherms and coefficient of determination ( $R^2$ ) for model fits

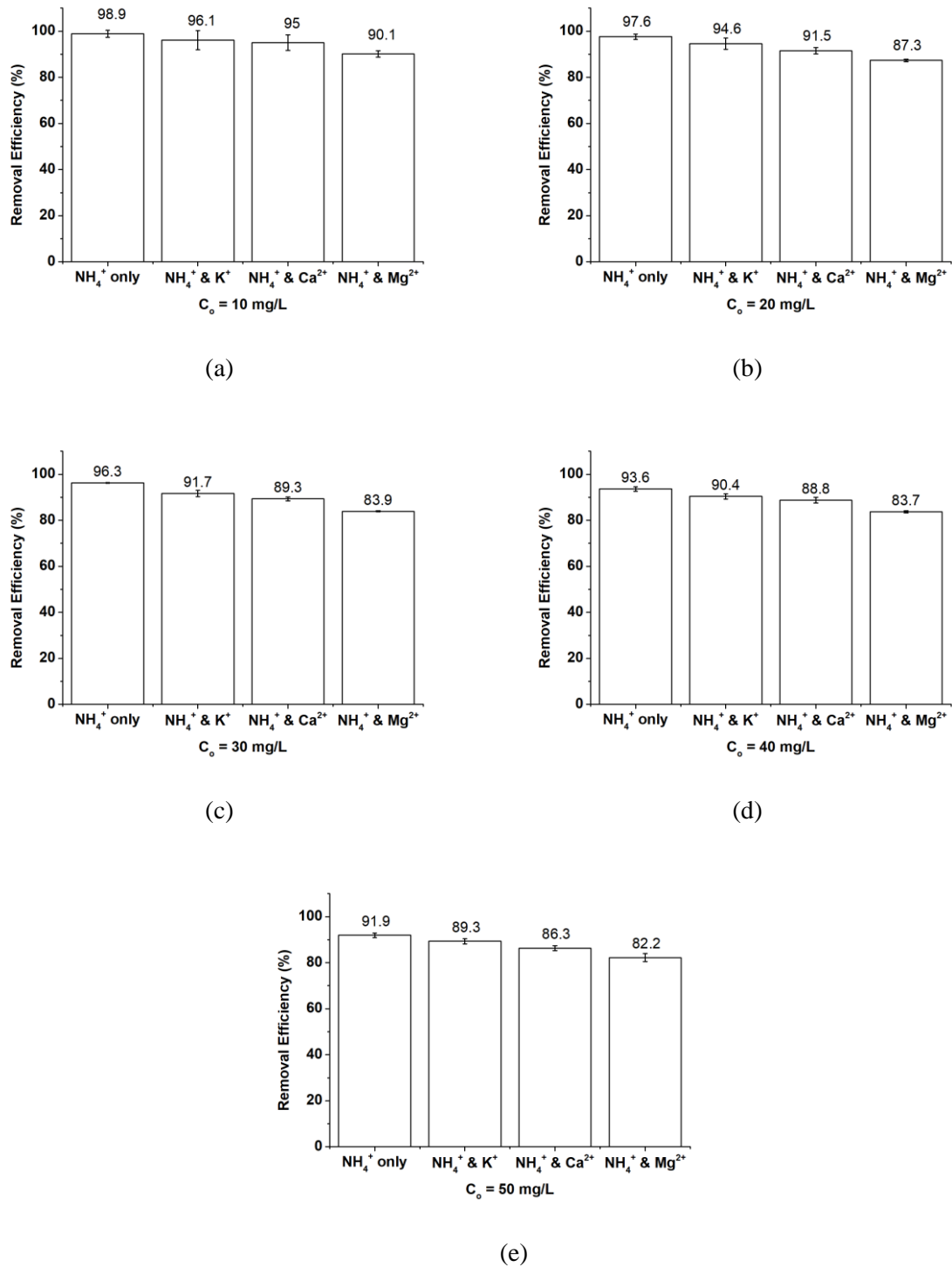
	Parameter values	$R^2$
Langmuir parameters		
K (L/mg)	0.0883	0.9752
b (mg/g)	18.37	
Freundlich parameters		
K ( (mg/g) (L/mg) <sup>1/n</sup> )	2.8567	0.9936
1/n	0.4433	



**Table 4** - Comparison of ammonium adsorption capacities of some natural and synthetic materials ( $C_o$  is initial ammonium concentration;  $Q_{max}$  is Langmuir maximum adsorption capacity)

Material	Solution pH	$C_o$ (mg/L)	$Q_{max}$ (mg/g)	Contact time	Reference
Purolite C100E	6.5	10 – 200	18.37	45 min	This study
Purolite C100E	6.5	50 - 2000	40.16	45 min	This study
Amberlite IR120 H	6.0	300 - 3000	29.76	30 min	<a href="#">Ding and Sartaj (2016)</a>
Purolite MN500	-	0 - 1000	$\approx 35$	4 days	<a href="#">Jorgensen and Weatherley (2003)</a>
Dowex 50w-x8	-	0 - 1000	$\approx 26$	4 days	<a href="#">Jorgensen and Weatherley (2003)</a>
Clinoptilolite	-	0 - 1000	$\approx 19$	4 days	<a href="#">Jorgensen and Weatherley (2003)</a>
Modified activated carbon with HNO <sub>3</sub>	8.0 – 9.0	685 - 735	19.34	20 min	<a href="#">Halim et al. (2013)</a>
Modified zeolite	6.0 – 7.0	50 - 250	22.64	5 hours	<a href="#">Wang et al. (2007)</a>

### 3.1.4. Effect of co-existing ions



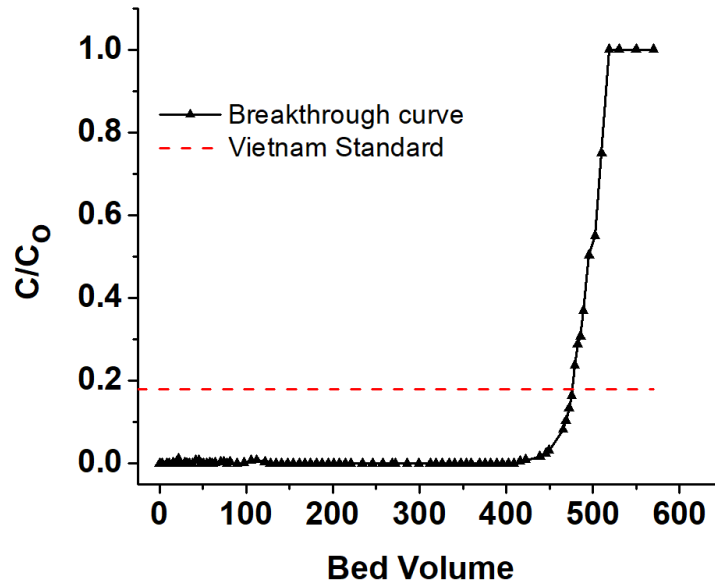
**Fig. 5** - Ammonium removal efficiency in the presence of potassium, calcium and magnesium ions at initial  $\text{NH}_4^+$  concentrations of (a) 10, (b) 20, (c) 30, (d) 40, and (e) 50 mg/L (resin dose = 10 g/L)

[Fig. 5](#) shows that the presence of co-existing cations (potassium, calcium, and magnesium ions) reduced the percentage of ammonium being removed, but only by less than 12%. The decrease followed the order,  $K^+ < Ca^{2+} < Mg^{2+}$ , which is the same order of equivalent concentrations of these cations (4.15 meq Mg/L, 2.5 meq Ca/L, and 1.3 meq K/L, respectively), although the same weight concentrations were used (50 mg/L). It is well known that in the ion exchange process, the affinity order of exchange between ions depends on their respective ion concentrations, expressed as the number of equivalents of ions per unit volume of solution and charge on the ion. The higher the charge on the ion, the greater the affinity of the resin to the ion. Therefore, another reason for the lowest degree of competition by  $K^+$  is the monovalent nature of this cation compared to the other two cations, which are divalent. However, being a monovalent ion, ammonium was still significantly adsorbed on the resin in the presence of divalent cations, calcium, and magnesium. The likely reason for this is that ammonium has a smaller hydrated ionic radius (0.331 nm) compared to calcium (0.412 nm) and magnesium (0.428 nm) ions ([Volkov et al., 1997](#)), which helped ammonium ions to make closer and better contact with the charged sites of the resin.

In addition to this, there would have been hydrogen bonding between the hydrogen atoms in ammonium and oxygen atoms in the resin helping this stronger adsorption. It can be seen that at low concentrations of ammonium, the influence of each competing ion on ammonium removal is minimal because the ion exchange capacity of the material (approximately 20 meq/L solution based on the manufacturer's value of 1.9 eq/L resin and 10 g resin/L solution used in the experiment) was not fully utilized by the cations (not all  $Na^+$  in the resin was exchanged). This means that the material can simultaneously exchange/remove both ammonium and co-ions without much competition between them. As the concentration of ammonium in the solution increased, the presence of competing ions reduced ammonium removal by a slightly higher percentage due to greater competition for the limited exchange sites. However, the reduction in ammonium removal did not exceed 12%, suggesting that ammonium has a high affinity towards the resin. The high affinity is due to the smaller hydrated ionic radius of ammonium and H-bonding, as already explained.

### 3.2. Fluidised bed studies

#### 3.2.1. Fluidised bed breakthrough curve



**Fig. 6** - Breakthrough curve for ammonium removal by Purolite C100-E resin in the fluidized bed study (Experimental conditions: resin weight: 75 g; influent ammonium concentration: 17.4 mg/L; filtration velocity: 0.5 m/h; the horizontal dotted line represents Vietnam’s ammonium concentration permissible limit for drinking water of 3 mg/L)

**Table 5** - Influent and effluent concentrations of other ions in solution

Metal ions	Zn (mg/L)	Mn (mg/L)	Fe (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)
Influent	0.07	0.022	0.25	20.2	10.8	0.216
Effluent	0.01	0.001	0.08	0.08	0.04	1.23

*Note: Detection limits ( $\mu\text{g/L}$ ) of Zn, Mn, Fe, Ca, Mg and Na are 0.01, 0.002, 0.593, 1.104, 0.048 and 0.106, respectively.*

[Fig. 6](#) depicts the breakthrough curve for ammonium removal by Purolite C100-E resin in the fluidised bed study. For the influent ammonium concentration of 17.4 mg/L, the total ammonium exchange during the operation time of 238 h (476 BV) was 786.35 mg which gives a maximum ion

exchange capacity ( $Q_{max}$ ) of 10.48 mg/g. This value is much higher than the column adsorption capacity of 3.3 mg/g reported for a zeolite (clinoptilolite) packed in a column with a height of 20 cm for the removal of ammonium from wastewater containing an ammonium concentration of 20 mg/L at a similar flow velocity (0.69 L/h) ([Hedström and Amofah, 2008](#)).

The maximum ammonium exchange capacity value in the fluidised bed study is lower than the batch Langmuir maximum capacity value for ammonium ( $Q_{max} = 18.37$  mg/g). One reason for this is that the synthetic solution used in the experiment was prepared from tap water, which contained many other metal ions competing with ammonium for exchange on the resin. [Table 5](#) shows the initial and effluent concentrations of some of the co-ions in the synthetic solution. As can be seen from this table,  $Ca^{2+}$  and  $Mg^{2+}$  concentrations decreased significantly after the solution passed through the column containing the resin, indicating that they have occupied the exchange sites in place of ammonium. The increase in  $Na^+$  in the effluent is due to  $Na^+$  ions in the resin exchanging with ammonium and other cations in the solution and entering the solution.

Other reasons for the poorer ammonium exchange capacity obtained in the fluidised bed study compared to the batch Langmuir maximum capacity value are: firstly, in the batch experiment, the exchange process reached equilibrium; and secondly, the Langmuir model predicted the maximum exchange capacity at a higher ammonium concentration in solution. These conditions were different in the fluidised bed experiment, where the exchange capacity was measured at lower ammonium concentration, and the exchange process did not reach equilibrium.

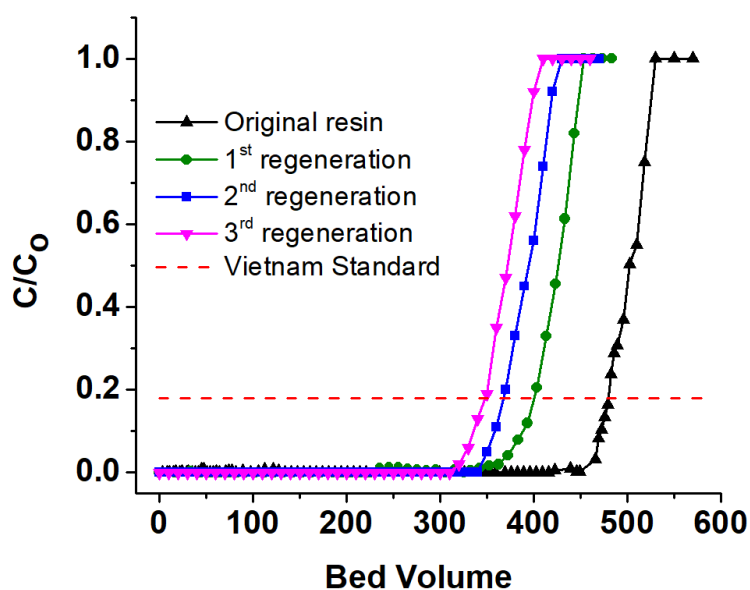
The fluidised bed ammonium ion exchange data fitted very satisfactorily to the Thomas model ( $R^2 = 0.9858$ ). The  $k_{Th}$  value obtained from the model fit was 0.1120 (ml/min mg), and the ammonium uptake per g of resin ( $q_o$ ) was 11.71 mg/g. This  $q_o$  value is approximately the same as that calculated manually from the experimental data ( $Q_{max} = 10.48$  mg/g).

[Table 6](#) displays the comparison of the maximum ammonium adsorption capacity obtained from the Thomas model, between the Purolite C100E resin in this study and some naturally-based materials. From [Table 6](#), it can be seen that Purolite C100-E resin has a higher adsorption capacity than the others, which means that this resin can be practically used to treat ammonium in aqueous solution.

**Table 6** – Comparison of the maximum ammonium dynamic sorption capacity of Purolite C100-E resin with other natural-based materials (calculated from the Thomas model)

Operation parameters				
Filtration velocity (m/h)	NH <sub>4</sub> <sup>+</sup> initial concentration (mg/L)	Detention time (h)	q <sub>0</sub> (mg/g)	Materials
0.51	17.4	0.53	11.71	This study
1.06	30	0.03	9.01	Peanut shell-based modified biochar ( <a href="#">Qiang et al., 2021</a> )
1.26	40	0.13	8.69	Corncob modified activated carbon ( <a href="#">Vu et al., 2018</a> )
1.22	25-50	0.33	3.9-5.32	Jordanian natural zeolite ( <a href="#">Mashal et al., 2014</a> )

### 3.2.3. Regeneration of Purolite C100E resin



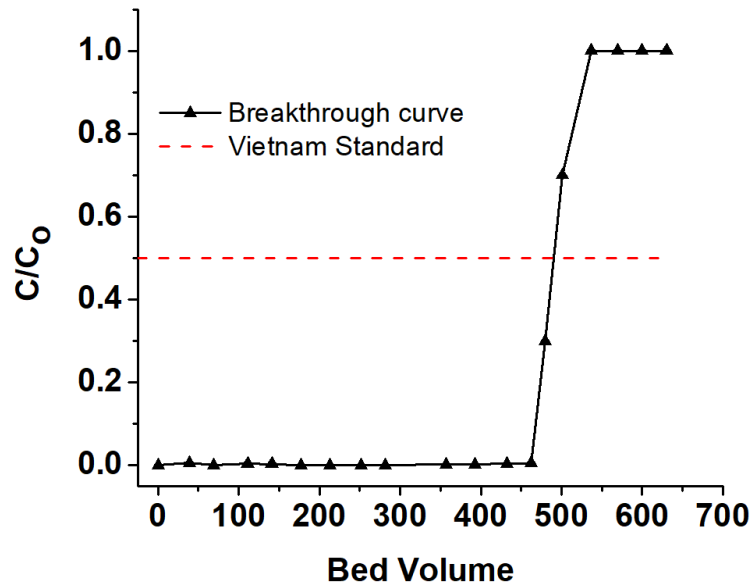
**Fig. 7** - Breakthrough curves for ammonium regeneration by 10% NaCl solution in the fluidised bed study (bed height = 27 cm, resin weight = 75 g, initial ammonium concentration = 17.4 mg/L, filtration velocity = 0.5 m/h) for three ion exchange – regeneration cycles of Purolite C100E; the horizontal dotted line represents Vietnam’s ammonium concentration permissible limit for drinking water of 3 mg/L

**Table 7** - Comparison of the performance of the original and regenerated Purolite C100E (volume of water treated was calculated as the volume of effluent passed through the column before reaching Vietnam’s ammonium concentration permissible limit for drinking water, resin weight = 75 g)

	Total ammonium exchange (mg)	Exchange capacity $Q_e$ (mg/g)	Volume treated (L)	Volume treated per kg material (L/kg)
Original resin	786.35	10.48	47.6	634.7
After 1 <sup>st</sup> cycle	711.75	9.49	45.4	605.3
After 2 <sup>nd</sup> cycle	684.44	9.12	43.0	573.3
After 3 <sup>rd</sup> cycle	659.90	8.79	41.0	546.7

The regenerated resin was tested for three adsorption-regeneration cycles. Results from [Table 7](#) display that the ammonium adsorbed on the resin after each cycle decreased, as shown by the shift in the breakthrough curves to lower bed volumes (to the left-hand side) in [Fig. 7](#). Therefore, the maximum exchange capacity for ammonium ( $Q_m$ ) of the resin in the column dropped progressively after each cycle. In the first cycle, the  $Q_m$  value decreased by 9.4% (from 10.48 to 9.49 mg/g). Nevertheless, the exchange capacity is still higher than many other materials ([Hedström and Amofah, 2008](#)), indicating that Purolite C100E resin can potentially eliminate ammonium in solutions having co-ions and is reusable for at least three times, thus reducing the cost of treatment.

### 3.3. Field trial with real contaminated water



**Fig. 8** - Breakthrough curve for ammonium removal by Purolite C100-E resin in the household filter (Experimental conditions: resin weight = 4000 g; bed height = 80 cm, filtration velocity = 1.9 m/h); the horizontal dotted line represents Vietnam's ammonium concentration permissible limit for drinking water of 3 mg/L

Based on the encouraging results of laboratory batch and fluidised bed experiments, a field trial was conducted in a household at Hoang Mai, Ha Noi, to treat ammonium in groundwater after the traditional sand filter pre-treatment (total resin weight of 4,000 g and flow rate of 15 L/h (corresponding to a filtration velocity of 1.9 m/h)). For the initial ammonium concentration of about 6 mg/L resulting from sand filtration, the total ammonium exchange in the resin was 14,068 mg, and the amount exchanged per unit weight of the resin ( $Q_{\max}$  value) was 3.52 mg/g for 164 h (492 BV) of filter operation (Fig. 8).

Compared to the laboratory fluidised bed experiment, the maximum ion exchange capacity value in the household filter operation is about 2.5 times lower (3.52 mg/g compared to 10.48 mg/g). There are two main reasons for this lower value. Firstly, the presence of many other metal ions at higher concentrations in the real groundwater than in the tap water used in the laboratory competed more with ammonium for ion exchange on the resin. Secondly, the field trial set-up was suspected of having a

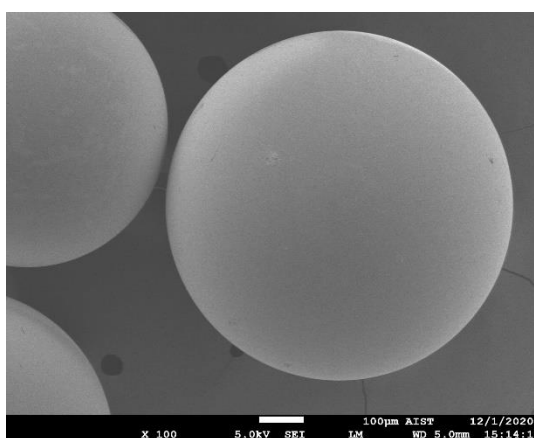


channeling effect, which could not be avoided because the inlet water entered the column near the edge of one side at the top of the column and passed through the resin layer to the bottom before exiting the column. This led to uneven distribution of the solution within the column, so not all solutions contacted the resin for ion exchange to remove ammonium.

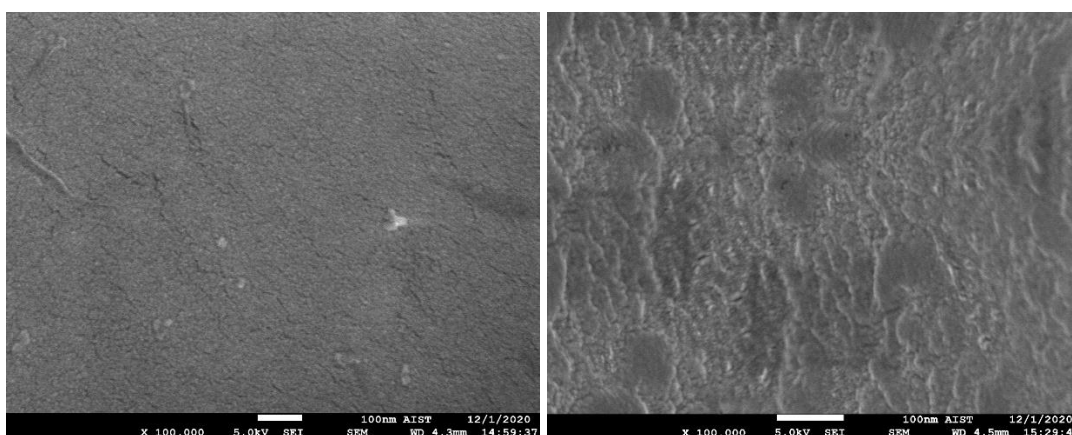
The household filter treated 492 BV of water (equivalent to 2460 liters of water) before it reached the Vietnamese ammonium concentration limit of 3 mg/L. Assuming that each household needs to use 15 L of treated water on an average per day (based on results of the pre-survey on water use demand of households in Ha Nam province), based on the results obtained, it can be estimated that each operating cycle can provide treated water (from groundwater with medium ammonium contamination of about 6 mg/L) for 164 days (2460/15) or more than five months.

According to a Purolite Engineering Bulletin document (2013), Purolite C100E resin can be regenerated and reused for at least five years. With the initial cost for purchasing resin being 10.0 US\$ (4 kg (resin weight in a household filter) x 2.5 US\$/kg) and industrial salt cost for regeneration process being 8.4 US\$ (12 cycles/5years (5 months use before one regeneration) x 2 kg /cycle x 0.35 US\$/kg salt), the total cost of operating the household filter cartridge to treat ammonium in groundwater for five years is about 18.4 US\$ (10 + 8.4). During this time, approximately 2460 L of contaminated groundwater which has the initial ammonium concentration of 6 mg/L can be treated before regenerating the material. It means that 29.5 m<sup>3</sup> (2460 L x 12 regenerating cycles x 1 m<sup>3</sup>/1000 L) of groundwater can be treated to meet the Vietnamese standard of drinking water quality, and the cost for each treated cubic meter of groundwater is as low as 0.62 US\$ (18.4/29.5).

### 3.4. Surface analysis



(a)



(b)

(c)

**Fig. 9** - Unreacted Purolite C100E resin particle (a) scale x100 and (b) scale x100,000; Reacted Purolite C100E resin particle (c) scale x100,000

**Table 8** - EDS analysis of the elemental composition of Purolite C100E resin before and after the exchange reaction

Element	Unreacted resin (wt%)	Reacted resin (wt%)
C	61.5	65.3
O	12.2	19.2
Na	7.6	2.8
N	0.0	4.4

The surfaces of Purolite C100-E particles were analyzed utilizing the SEM method before and after the ion exchange process. SEM images of the unreacted and reacted resin particles are shown in [Fig. 9](#). As can be seen from these depictions, prior to the ion-exchange reaction, the surface of resin particles was quite smooth ([Fig. 9a](#) and [9b](#)). After the reaction ([Fig. 9c](#)), uneven surfaces were seen, probably as a result of ammonium adsorption.

The EDS analysis was conducted to determine the elemental composition of the resin before and after the exchange reaction. Results show that Na concentration decreased while N concentration increased after the reaction, thus confirming that  $\text{NH}_4^+$  (represented by N in EDS analysis) has been exchanged with  $\text{Na}^+$  in the resin ([Table 8](#)). Before the reaction, the sodium content in the resin was 7.6%, while the nitrogen content of the material was approximately zero. After the reaction, the sodium content dropped by 4.8%, meanwhile nitrogen content increased by 4.4%. This is the same as a sodium content decrease of 0.21 meq/100 g and an ammonium content increase of 0.31 meq/100 g. These figures do not indicate a 1:1 exchange in terms of charge balance between the two cations. The excess ammonium adsorbed on the resin may be a result of processes other than electrostatic adsorption, such as H-bonding. [Sica et al. \(2014\)](#) also reported that ammonium exchange with sodium on Purolite C150H did not occur on a 1:1 equivalent basis. Using EDS measurement, they found that 0.39 equivalent units of sodium was replaced by 1.13 equivalent units of ammonium and explained the higher amounts of ammonium adsorption as due to its adsorption on a low polar surface. Another reason for the unequal equivalents of exchange between the two cations could be because EDS - which measures the concentrations only on surface layers of a few micrometers of adsorbent - is not entirely reliable in providing accurate concentrations of the adsorbed ammonium and sodium ([Kalaruban et al., 2016](#)).

#### **4. Conclusions**

This study shows that the cation exchange resin Purolite C100E can remove ammonium from contaminated water, effectively applying a wide pH range from 3 to 8. Most of the ammonium was exchanged rapidly on the resin within a contact time of 10 min, and the exchange process reached equilibrium at around 45 min. Both Pseudo-first order and Pseudo-second order models can be applied

to describe the kinetics of the exchange process. Equilibrium exchange data fitted with both Langmuir and Freundlich isotherm models. The Langmuir maximum exchange capacity calculated based on data from an experiment using low ammonium concentrations in solution (typical of most contaminated groundwaters) was 18.37 mg/L. However, when high initial concentrations were used, this capacity increased to 40.16 mg/L, which is higher than most of the values reported in the literature for many synthetic and natural resins. On a weight basis, magnesium ion in the solution reduced ammonium exchange the most among the co-ions tested, followed by calcium and potassium. However, the reduction in ammonium exchange was <12%. Such low percentage reduction is explained as due to the high affinity of ammonium to the resin resulting from hydrogen bonding and low hydrated ionic radius of ammonium.

The results from fluidised bed studies using synthetic water reveal that Purolite C100E resin has good potential to treat several bed volumes of contaminated water by maintaining the effluent ammonium concentration below the Vietnam drinking water standard. The breakthrough data was satisfactorily described by the Thomas model. The used fluidised bed can be regenerated using NaCl leaching at least three times and reused without losing much of the exchange capacity for ammonium, thus the operating cost can be reduced significantly. In a household field trial test lasting one week, the resin could reduce the ammonium concentration in groundwater after sand filtration pretreatment continuously to below the Vietnam permissible concentration. A cost analysis on the use of Purolite C100E resin for the treatment of a typically contaminated groundwater (6 mg/L of ammonium) demonstrated that the cost for treating each cubic meter of groundwater could be as low as 0.62 US\$.

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