Selective removal of nitrate using a novel asymmetric amine based strongly basic anion exchange resin

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Abstract
In this study, a novel asymmetric amine-based strongly basic anion exchange resin SE-1 was synthesized successfully via the reaction of chloromethylated styrene–divinylbenzene copolymer with N,N-dimethyloctylamine. The sorption performance of SE-1 for selective removal of nitrate in aqueous solution was compared to a commercially available nitrate specialty resin, namely Purolite A 520E (A 520E). It was found that the kinetic data could be described better by the pseudo-second-order model, and SE-1 indicated a faster sorption kinetics than A 520E resin. The Langmiur model was more appropriate for explicating the sorption isotherm. Importantly, SE-1 exhibited a greater sorption capacity for nitrate regardless of the absence or presence of competing anions in solutions. The result of column tests reinforced the feasibility of SE-1 for practical application in groundwater treatment.
Keywords
Nitrate, selectivity, anion exchange resin, removal, groundwater

Introduction
Nitrate contamination in surface water and groundwater is an increasingly serious problem in all over the world (Bergquist et al., 2016; Knoll et al., 2019). The presence of excess nitrate in drinking water can cause enlargement of the thyroid gland and form a potential human carcinogen (Hunault et al., 2007; Zhang et al., 2013). In addition, nitrate can be reduced into nitrite and combine with ferrous ions of hemoglobin in blood to form methemoglobin, leading to methemoglobinemia, which is fatal to infants (Rao et al., 2019). Background nitrate concentrations in surface waters are usually below 5 mg/L, but groundwater nitrate contamination is a severe issue in developing countries, where higher nitrate content is frequently detected in groundwater (Beltrán de Heredia et al., 2006; Liu et al., 2019). In view of the fact that groundwater has been widely used for agricultural and industrial productions, it is of vital importance for the removal of nitrates from wastewater (Gu et al., 2018).

In the recent years, a variety of traditional nitrate treatments, such as biological denitrification, membrane separation, ion exchange, sorption and chemical reduction have been presented (Epsztein et al., 2015; Hekmatzadeh et al., 2013; Li et al., 2016; Shi et al., 2016; Wu et al., 2019; Zhang et al., 2016). Among these methods, ion exchange has been verified to be an effective technology to remove inorganic anions such as nitrate from aqueous solutions due to its simplicity and relatively lower costs (Hekmatzadeh et al., 2012). Nitrate can be strongly adsorbed on some commercially available conventional strong basic anion exchange resins (Dron and Dodi, 2011; Malika et al., 2010). However, groundwater mostly contains not only nitrate but also relatively high concentrations of competing anions such as sulfate, chloride and bicarbonate ions. Particularly, sulfate is a divalent anion which is preferentially adsorbed by conventional strongly basic anion exchangers through an electrostatic interaction, leading to a sharp reduction of the resin sorption capacity for nitrate, as it is a monovalent ion (Pakzadeh and Batista, 2011). The subsequently developed strongly basic anion exchangers are nitrate-specialty resins such as Purolite A 520E (A 520E), Imac HP55, Amberlite IRA 996 and Indion NSSR (Hekmatzadeh et al., 2012). These nitrate specialty resins are functionalized by reaction with triethylamine to create quaternary ammonium exchange sites in place of shorter chain trimethylamine as an amination reagent for the conventional resins. In other words, all of the three methyl groups of trimethylamine have been lengthened. As a result, the nitrate selectivity of the specialty resin is improved, but the sorption kinetics and capacity of the resin are decreased (Bonnesen et al., 2000).

To overcome such drawbacks, in this study, a novel strongly basic anion exchange resin SE-1 is synthesized by the reaction of macroporous chloromethylated styrene–divinylbenzene copolymer with N,N-dimethyloctylamine, which exclusively increases one of the methyl groups of trimethylamine to octyl group, forming an asymmetric tertiary amine as the amination reagent. Theoretically, the long-carbon side-chain benefits for
selectivity and the short chain can enhance kinetics and capacity towards nitrate of the resin. Its physical properties were characterized, and the sorption ability of this new resin for nitrate was investigated. The A 520E resin was selected as the baseline resin for comparison because it is currently in wide use for treating groundwater. To the best of our knowledge, the preparation and application of this asymmetric amine-based strongly basic anion exchange has never been reported.

**Materials and methods**

**Materials**

Macroporous chloromethylated polystyrene-divinylbenzene (Cl-PS-DVB) precursor resin (cross-linking density 6%, chloride content 18%) was kindly provided by Jiangsu NanGe Environmental Technology Co., Ltd (China). The nitrate specialty anion exchange resin, Purolite A 520E (A 520E) in the chloride form, was purchased from Aladdin Chemistry Co., Ltd (China). Mainly, triethylamine functional groups are attached on the A520E resin with a macroporous polystyrene matrix, and its total anion-exchange capacity is 2.8 mmol/g. N, N-dimethyloctylamine and other reagents were obtained from Nanjing Reagent Co., Ltd (China).

**Preparation and characterization of SE-1**

The strongly basic anion exchange resin SE-1 was synthesized according to a proprietary technique proposed by our laboratory (Sun et al., 2015). In brief, procedure for SE-1 preparation is exhibited in Scheme 1. Twenty grams of Cl-PS-DVB beads were swollen in 50 g of benzene, which was stirred in a 250 mL flask equipped with a mechanical stirrer, a thermometer and a reflux condenser at 303 K overnight. Afterwards, the swollen polymer particles were filtered out of the suspension. A solution comprised of 40 g of N, N-dimethyloctylamine and 40 g of ethanol was then gradually added, and the mixture was stirred at 338 K for 8 h. Finally, the residual reaction solution was filtered out, and the strongly basic anion exchanger SE-1 was obtained. After the reaction was complete, the resulting resin was washed alternatively with 1.0 M HCl, followed by deionized water till neutral pH and extracted for 8 h with anhydrous ethanol and was finally dried at 318 K under vacuum to constant weight. The obtained resin SE-1 was characterized by Fourier transform infrared spectrometer (FT-IR; Nicolet 5700, USA) and N\textsubscript{2} sorption analysis (ASAP-2010C, Micromeritics, USA). The total anion exchange capacity for the resin was measured by performing a Mohr titration on the Cl\textsuperscript{−} ion replaced when resin was treated with excess NaNO\textsubscript{3}.

![Scheme 1. Synthesis route of SE-1.](image-url)
Batch sorption tests

The experimental procedures of batch sorption were performed according to the previous studies (Bhatnagar and Sillanp, 2011; Li et al., 2019a, 2019b). About 0.1 g of dry resin was introduced into 100 mL aqueous solutions with different concentrations of nitrate. The flasks were completely sealed, placed in a constant temperature shaker at desired temperature and shaken at 150 r/min for 24 h to ensure the sorption process reaching equilibrium. The solution pH was gained by adding dilute HCl or NaOH solutions, and Na₂SO₄, NaCl or NaHCO₃ was added into the solution to study the effect of coexisting anions. For sorption kinetics, a weighed sample of resin (0.5 g) was introduced into 100 mg/L nitrate solution (500 mL) and agitated at 150 r/min under 303 K continuously. A 0.5 mL aliquot of solution was withdrawn from the flasks at various time intervals to determine the sorption kinetics. The concentration (Cₐ, mg/L) of the residual aqueous phase was determined using a UV–vis spectrophotometer (Agilent 8453, USA). The equilibrium sorption capacity (Qₑ, mg/g) was calculated as follows

\[
Qₑ = \frac{(C₀-Cₑ)V}{W}
\]

where \(C₀\) is the initial nitrate concentration (mg/L), \(W\) is the mass of resin (g) and \(V\) is the volume of solution (L).

Column sorption–elution experiments

Considering the practical sorption process in wastewater treatment plant, dynamic behavior of SE-1 in fixed-bed column is necessary for the feasibility of removal nitrate from actual wastewater (Zietzschmann et al., 2016). Dynamic column experiments were conducted that a 10 mL portion of resin was packed into a glass column (18 mm × 200 mm) equipped with a water bath to maintain a constant temperature. All the column sorption experiments were performed with a simulated nitrate-contaminated groundwater prepared by dissolving the definite amount of NaNO₃, MgSO₄, CaCl₂ and NaHCO₃ in the deionized water. Chemical compositions of the simulated groundwater are provided in Table 1, which was selected according to Cao et al.’s work based on the analysis results of the contaminated groundwater from Zhangqiu city, Shandong Province, China (Cao et al., 2011). The model solutions were pumped and up-bottom passed to the column at a constant rate of 20 bed volume per hour (BV/h) using a peristaltic pump at the temperature of 298 K. The saturated resin was eluted with 0.8 M NaCl solution at 298 K, and the flow rate was controlled at 5 BV/h.

Results and discussion

Characterization of SE-1 resin

The FT-IR spectra of chloromethylated PS-DVB copolymer and SE-1 are shown in Figure 1. In the spectra of chloromethylated PS-DVB, two strong sorption bands at

| Species | Ca²⁺ | Mg²⁺ | Na⁺ | NO₃⁻ | SO₄²⁻ | Cl⁻ | HCO₃⁻ |
|---------|------|------|-----|------|-------|-----|-------|
| Content (mg/L) | 150 | 62.5 | 168.5 | 200 | 250 | 266.3 | 250 |
1265 and 675 cm$^{-1}$ were ascribed to C–H bending vibration of CH$_2$Cl and C–Cl, respectively. The disappearance of both the peaks in SE-1 implied that effective interaction between N,N-dimethyloctylamine and CH$_2$Cl/C–Cl group has occurred (Betilha et al., 2016). In addition, the peak at 1483 cm$^{-1}$ assigned to the stretching vibration of C–N group was found in the spectra of SE-1. These different characteristic peaks of chloromethylated PS-DVB and SE-1 as well as the total exchange capacity of 3.0 mmol/g confirmed the successful synthesis of the novel resin. Furthermore, a new peak at 1383 cm$^{-1}$ ascribed to the N–O asymmetric stretching was observed after nitrate sorption, confirming that the nitrate could be adsorbed onto SE-1 (Diniz et al., 2017).

Figure 2 presents the sorption–desorption isotherms of nitrogen at 77 K on SE-1. The isotherms show a Type IV profile according to the IUPAC classification with remarkable hysteresis loops in relative pressure higher than 0.9. This implies that the pores comprising the resin sample are mostly mesoporous and macroporous, which is preferred from the adsorbate diffusion point of view (Ling et al., 2010). The values of BET surface area and BJH desorption average pore diameter calculated from the basis of the nitrogen sorption data were 23.1 m$^2$/g and 31.0 nm, respectively.

**Effect of contact time and sorption kinetics**

Figure 3 shows the plot of nitrate uptake versus contact time for SE-1 and A 520E. The kinetic curves revealed that the sorption was fast in the initial 60 min and then gradually reached equilibrium. The maximum amount of nitrate adsorbed onto SE-1 was found higher than that on A 520E when the sorption equilibrium reached.

![Figure I. The FTIR spectra of Cl-PS-DVB and SE-1.](image-url)
Figure 2. Nitrogen sorption–desorption isotherms of SE-1 with inset showing the corresponding pore size distribution.

Figure 3. Sorption kinetics of SE-1 and A 520E.
To understand the sorption mechanism in the nitrate sorption process, the experimental data were fitted with three common kinetic models, namely pseudo-first-order equation (equation (2)), pseudo-second-order equation (equation (3)) and intraparticle diffusion equation (equation (4)) (Fu et al., 2015; Saki et al., 2019)

\begin{equation}
Q_t = Q_e \left(1 - e^{-k_1t}\right)
\end{equation}

\begin{equation}
Q_t = \frac{k_2Q_e^2t}{1 + k_2Q_et}
\end{equation}

\begin{equation}
Q_t = k_{ipd}t^{0.5} + C
\end{equation}

where \(Q_e\) and \(Q_t\) are the sorption amount (mg/g) at equilibrium and at time \(t\) (min), respectively; \(C\) (mg/g) is a constant; while \(k_1\) (1/min), \(k_2\) (g/mg/min) and \(k_{ipd}\) (mg/g/min\(^{0.5}\)) are the rate constants for the pseudo-first-order, pseudo-second-order and intra-particle diffusion equations, respectively. The correlation parameters and coefficients \((R^2)\) are listed in Table 2.

According to the fitting parameters listed in Table 2, the sorption processes onto both SE-1 and A 520E were well-fitted with pseudo-second-order model because of the higher \(R^2\) values, and the calculated equilibrium sorption capacities (\(Q_e, cal\)) were close to the experimental ones (\(Q_e, exp\)). This indicates that the chemical sorption process determines the rate of nitrate sorption onto both the resins. In the pseudo-second-order kinetics model, \(h = k_2Q_e^2\) (mg/(g min)) is defined as the initial sorption rate constant, and the value of \(h\) as well as \(k_2\) for SE-1 is larger than that of A 520E, suggesting that SE-1 possesses faster kinetics. It has been observed that increasing the number of carbon atoms in alkyl chain of amino group on a resin could result in a decrease in the sorption rate for some inorganic anions like \(\text{TeO}_4^-\) and \(\text{ClO}_4^-\) (Cul et al., 1993; Tripp and Clifford, 2000). The total carbon number in alkyl chain of amino group on SE-1 is larger than that of A 520E, but SE-1 has a better sorption kinetic property. Moreover, the amount of nitrate onto SE-1 was larger than that of A 520E at the equilibrium state, which indicated that the two short-carbon chains (methyl groups) on the exchange sites of SE-1 played a significant role in promoting kinetics and enhancing capacity (Gu et al., 2000).

### Effect of competing anions and sorption selectivity

Generally, the common inorganic anions such as \(\text{SO}_4^{2-}\), \(\text{Cl}^-\) and \(\text{HCO}_3^-\) often coexist with \(\text{NO}_3^-\) in natural water sources, which can act as competing ions and strongly interfere with sorption process of \(\text{NO}_3^-\), resulting in inefficiency. Therefore, a potential adsorbent should

#### Table 2. Kinetic parameters obtained from the three kinetics models at 303 K.

| Resin     | \(Q_e,exp\) | \(Q_e,cal\) | \(10^2k_1\) | \(R^2\) | \(Q_e,cal\) | \(10^4k_2\) | \(h\) | \(R^2\) | \(k_{ipd}\) | \(R^2\) |
|-----------|-------------|-------------|-------------|--------|-------------|-------------|------|--------|-------------|--------|
| SE-1      | 135.4       | 81.5        | 3.01        | 0.9571 | 148.0       | 5.39        | 11.79| 0.9981 | 10.12       | 0.8489 |
| A 520E    | 118.8       | 84.0        | 2.58        | 0.9819 | 132.0       | 4.02        | 7.00 | 0.9976 | 7.79        | 0.8102 |

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have a high selectivity towards nitrate. Figure 4 illustrates the effect of coexisting SO$_4^{2-}$, Cl$^-$ and HCO$_3^-$ on NO$_3^-$ sorption onto the resins from aqueous solutions.

As seen in Figure 4, increasing the coexisting anion concentration would lead to an obvious decrease in nitrate sorption capacity on both the resins, which would result from the competitive effect of anions for available sorption sites of resins. Compared with A 520E resin, SE-1 had a relatively large nitrate uptake in the presence of the competing anions and exhibited enhanced selectivity for nitrate. Taking into account their same PS-DVB matrix, varying adsorbed amounts of the two resins could be attributed to the functional groups of the resins. To further quantify the selectivity of the tested resins, the distribution coefficient $K_d$ (in L/g) was determined by the following equation (Gao et al., 2008)

$$K_d = \frac{Q_e}{C_e}$$

where $Q_e$ (mg/g) is the equilibrium binding amount and $C_e$ (mg/L) is the equilibrium concentration. Table 3 revealed that the values of $K_d$ for SE-1 and A 520E gradually reduced with the increase of each coexisting anion concentration. SE-1 exhibited higher $K_d$ values than A 520E at the same concentration of competitive anion in aqueous solution, indicating that SE-1 has the enhanced selectivity for nitrate. For example, the $K_d$ values of SE-1 were about 60%, 40% and 36% at 200 mg/L of SO$_4^{2-}$, Cl$^-$ and HCO$_3^-$, while around 100%, 58% and 34% when each coexisting anion content increased to 600 mg/L, which were obviously higher than those of A 520E resin, respectively. This could be explained as the long-chain octyl functional groups on quaternary ammonium structure make SE-1 more hydrophobic and thus more selective in adsorbing nitrate than the tested coexisting anions with a higher hydration energy (Smith, 1977; Song et al., 2012). The excellent selectivity for nitrate of SE-1 suggested that the novel asymmetric amine-based exchanger was more effective than A 520E resin in removing nitrate from a solution containing high levels of competing common inorganic anions.

**Effect of pH**

A range of initial solution pH from 3 to 10 was applied to investigate the effect of pH solution on nitrate sorption by SE-1 at 298 K is illustrated in Figure 5. In fresh water,
the pH value appears to have a slight effect on the sorption capacity and the nitrate uptake of SE-1 varying from 84.1 to 91.6 mg/g in the pH range from 3 to 11. Without adjusting the pH value of the solution, the operating pH of the solution was 6.2 at which the maximum nitrate sorption occurred. This phenomenon was also observed during the sorption of nitrate onto some other strongly basic exchangers (Milmile et al., 2011; Song et al., 2012). The main reason for the marginal decrease in nitrate uptake with the pH variation on both acidic and basic sides was presumed to be due to the competition between nitrate and chloride ion originating from pH adjustment process for active sites on the resin (Milmile et al., 2011). To confirm this assumption, the test of effect of pH on sorption capacity in the presence of 600 mg/L chloride ion for shielding the small change of anion content in solution was further carried out. As can be seen from Figure 5, there is almost no change in the nitrate uptake with the pH varying from 3 to 11 for SE-1 in the solution with 600 mg/L chloride ion. The result exposes that the sorption property of SE-1 towards nitrate is stable in the tested pH range, which makes it suitable for practical application at different places where the pH of the water changes.

Table 3. Nitrate distribution coefficients $K_d$ (L/g) in different concentration of coexisting anions.

| Resin   | $\text{SO}_4^{2-}$ (mg/L) | $\text{Cl}^-$ (mg/L) | $\text{HCO}_3^-$ (mg/L) |
|---------|---------------------------|-----------------------|-------------------------|
|         | 200           | 400       | 600                   | 200       | 400       | 600       | 200       | 400       | 600       |
| SE-1    | 2.62          | 2.11      | 1.90                  | 2.26      | 1.56      | 1.14      | 3.44      | 2.58      | 2.06      |
| A 520E  | 1.64          | 1.04      | 0.95                  | 1.62      | 0.97      | 0.72      | 2.53      | 1.85      | 1.54      |

Figure 5. Effect of pH on nitrate sorption for SE-1 in the absence and presence of chloride ion.
Sorption isotherms

The nitrate sorption isotherms at three different temperatures on SE-1 are displayed in Figure 6. The amount of nitrate adsorbed on SE-1 increased with increasing equilibrium concentration and decreasing temperature. The Langmuir (equation (6)) and Freundlich (equation (7)) models which are two typical isotherms for describing the sorption on adsorbent from aqueous solution were employed to further describe the sorption isotherms (Li et al., 2017; Manjunath and Kumar, 2018)

\[
Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}
\]  \hspace{1cm} (6)

\[
Q_e = K_F C_e^{1/n}
\]  \hspace{1cm} (7)

where \(Q_e\) (mg/g) is the sorption amount at equilibrium and \(Q_m\) (mg/g) is the maximum sorption amount; \(K_L\) (L/mg) and \(K_F\) (L/g) are constants of the Langmuir and Freundlich models, respectively.

As tabulated in Table 4, the sorption isotherms could be described by both the models. Whereas, Langmuir equations were more reliable than Freundlich equations because all the correlation factors (\(R^2\)) of the former were larger than the latter. This indicates that the nitrate sorption on SE-1 was monolayer, and it has taken place at specific sorption sites (Manjunath and Kumar, 2018). When the temperature decreases, the maximum sorption capacity of SE-1 calculated by the Langmuir equation increases a little, which is a special characteristic of electrostatic interaction between negatively charged nitrate and positively charged quaternary amine group on the resin without any notable effect with temperature. Additionally, Table 5 lists the calculated maximum \(\text{NO}_3^-\) sorption capacities of SE-1 and

![Figure 6. Sorption isotherms of nitrate on SE-1.](image-url)
the other adsorbents. It was seen that SE-1 exhibits better sorption ability for nitrate than most of these materials.

**Fixed-bed column study**

A simulated groundwater solution was allowed to pass through the column, and the breakthrough curves of nitrate obtained by SE-1 and A 520E were depicted in Figure 7.

Table 4. Parameters of Langmuir and Freundlich models for the nitrate sorption onto SE-1.

| T/K  | Langmuir equation | Freundlich equation |
|------|------------------|---------------------|
|      | Q_\text{m} (mg/g) | K_L (L/mg) | R^2 | n | K_F | R^2 |
| 283  | 144.9            | 0.413   | 0.9967 | 4.50 | 58.57 | 0.9753 |
| 298  | 138.9            | 0.350   | 0.9944 | 5.21 | 59.57 | 0.9848 |
| 313  | 137.0            | 0.225   | 0.9933 | 3.86 | 45.36 | 0.9971 |

Table 5. Comparison of the maximum sorption capacities toward nitrate by different materials reported in literature and in this work.

| Adsorbents                  | Q_\text{m} (mg/g) | T (K) | References             |
|-----------------------------|-------------------|-------|------------------------|
| Magnetic amine-crosslinked biopolymer | 65.4               | 298   | Song et al., 2016       |
| La (Lanthanum)-biochar      | 100.0             | 298   | Wang et al., 2015       |
| Magnetic anion-exchange resin | 108.5             | 293   | Wang et al., 2016       |
| D201 resin                  | 38.5              | 293   | Song et al., 2013       |
| Purolite A 300 resin        | 147.4             | 293   | Song et al., 2012       |
| SE-1                        | 138.9             | 298   | This work               |

Figure 7. Breakthrough curves of nitrate obtained by SE-1 and A 520E using model solution.
The maximum contaminant level of nitrate concentration (44 mg/L) in drinking water set by USA and China in the effluent was also shown by the dashed horizontal line in the graph. This limited content of nitrate for SE-1 and A 520E was reached at bed volumes (BV) of 200 and 150, respectively. In other words, the former processed over 30% more BVs than the latter. In addition, as displayed in Figure 7, it took about 500 and 350 BVs for SE-1 and A 520E, respectively, to reach complete sorption saturation. These results indicate that SE-1 possesses superior adsorptive properties, which can be explained by its higher nitrate selectivity resulting from its unique chemical structure. The 0.8 M NaCl solution was employed for the desorption of nitrate from saturated resins, and the elution curve of nitrate obtained by SE-1 was displayed in Figure 8. It can be seen that nitrate loaded onto SE-1 can be well recovered by 25 BV of NaCl solution with the corresponding desorption efficiency above 98%, and the similar regeneration result was obtained for saturated A 520E resin. In other words, consuming the same amount of brine for resin regeneration, SE-1 can treat more volumes of simulated groundwater, thereby reducing the overall operational costs.

**Conclusion**

A novel asymmetric amine-based strongly basic anion exchanger SE-1 was successfully synthesized by the reaction of chloromethylated PS-DVB copolymer with \(N, N\)-dimethyloctylamine for nitrate removal. A commercially available nitrate specialty resin Purolite A 520E (A 520E) was chosen for the comparison purpose. SE-1 exhibited a greater sorption capacity for nitrate regardless of the absence or presence of competing anions in solutions and demonstrated faster sorption kinetics performance than A 520E. Thus, SE-1 might be a potential alternative adsorbent in purification of practical nitrate-polluted drinking water resources.

**Figure 8.** Elution curves of nitrate obtained by SE-1 with inset showing the curves by A 520E.
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