Adsorption of Nitrate by a Novel Polyacrylic Anion Exchange Resin from Water with Dissolved Organic Matters: Batch and Column Study

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Featured Application: The novelty of this work is that the prepared resin AEE-3 has a potential application in the removal of nitrate from real secondary treated wastewater containing dissolved organic matters.

Abstract: A novel anion exchange resin AEE-3 was synthesized by N-alkylation of a weakly basic polyacrylic anion exchanger D311 with 1-bromopropane to effectively remove nitrate (NO$_3^-$-N) from aqueous solution. The related finding revealed that its adsorption isotherm obeyed the Langmuir model well, and the second-order model was more validated for the NO$_3^-$-N adsorption kinetics study. Compared to commercially-available polystyrene-based nitrate specialty resin Purolite A 520E (A520E), AEE-3 resin has a higher adsorbed amount and better regeneration performance toward NO$_3^-$-N in the existence of dissolved organic matter (DOM) using static and dynamic methods. Notably, a real secondary treated wastewater (STWW) obtained from a local municipal wastewater treatment plant was also assessed for NO$_3^-$-N removal in fixed-bed columns. Observations from this study indicated that AEE-3 could effectively remove NO$_3^-$-N from contaminated surface water.

Keywords: nitrate; dissolved organic matter; ion exchange; selectivity

1. Introduction

With the rapid development of industry and agriculture, excessively-used nutrients such as nitrogen (N) and phosphorous (P) in crop production have been infiltrated into rivers, lakes and ponds, leading to the eutrophication of aquatic systems [1,2]. Nowadays, nitrate (NO$_3^-$-N) pollution in surface and ground water is a severe environmental problem due to its carcinogenicity, toxicity and potential hazards to human health and livestock. Therefore, the World Health Organization (WHO) set the NO$_3^-$-N concentration limit of 50 mg/L, whereas the U.S. Environmental protection Agency (U.S. EPA) allows 10 mg/L in drinking water [3,4].

Current approaches like reverse osmosis, electrodialysis, biological denitrification, adsorption and ion exchange have been utilized to treat NO$_3^-$-N polluted water [5,6]. In consideration of the merits of ion exchange, such as high efficiency, acceptable regeneration and cost-effective preparation, anion exchange resins (AERs) have been employed to adsorb NO$_3^-$-N from contaminated water [7–9]. On the basis of their chemical structure, commercial AERs are normally categorized into two skeletons, namely, polystyrene and polyacrylic. Polystyrene AERs have been used to effectively adsorb NO$_3^-$-N from ground water in the past decade [10,11]. However, high concentrations of dissolved organic matters (DOMs) always exist in surface water, including secondary treated wastewater (STWW),
and can engender a strong affinity for resins via electrostatic attraction, hydrophobic interaction and so on [12–14]. Hence, AERs are more sensitive to fouling with DOMs, which would compete with NO$_3^-$-N for the active sites and cause the decrease in NO$_3^-$-N adsorption. More seriously, coexisting DOM could lead to an irreversible fixation to anion exchangers. Polyacrylic AERs with hydrophilic structures reveal a stronger resistance to organic fouling performance than polystyrene AERs [15]. Moreover, acrylic-based resins possess unique physiochemical properties, rapid adsorption rates and high ion-exchange capacities [16,17]. Accordingly, polyacrylic AERs could serve as a promising absorbent to effectively remove NO$_3^-$-N from polluted water in the presence of DOMs. Nevertheless, few works have shown the feasibility of polyacrylic resins for NO$_3^-$-N removal in real STWW containing NO$_3^-$-N at high levels.

However, competitive anions such as chloride (Cl$^-$) or sulfate (SO$_4^{2-}$) exist widely in water, which can weaken NO$_3^-$-N uptake efficacy of AERs [18]. To circumvent this limitation, studies have been devoted to preparing a novel anion exchanger with prominent selectivity toward NO$_3^-$-N. The long alkyl chain addition at the exchange sites of resins could be of great benefit for the preferable selectivity toward monovalent anions because of its steric hindrance and hydrophobic effect [19,20]. Hence, it is intriguing for us to modify the weakly basic resin by introducing long alkyl groups around the active amine groups, which can easily form strongly basic functional groups (quaternary ammonium) which interact with NO$_3^-$-N through strong electrostatic attraction.

Herein, a weakly basic polyacrylic anion exchanger D311 was modified with 1-bromopropane (C$_3$H$_7$Br) to prepare a strongly basic anion exchanger AEE-3 with high efficiency and brilliant selectivity for NO$_3^-$-N uptake. The adsorption kinetics, isotherms, influence of pH value and competitive anions were investigated. In addition, commercial nitrate-selective polystyrene resin Purolite A 520E (A520E) was chosen to make a comparison with AEE-3 in both batch and fixed-bed column experiments, further demonstrating that AEE-3 is more resistant to fouling by DOMs (humic acid, tannic acid and sodium dodecyl benzene sulfonate). Also, a dynamic experiment was studied to evaluate the adsorption performance of AEE-3 toward NO$_3^-$-N in real STWW.

2. Materials and Methods

2.1. Material

A commercially-available weakly basic anion exchanger D311 and strongly basic anion exchanger Purolite A 520E (A520E) were obtained from Huizhu Resin Co., Ltd. (Shanghai, China) and Purolite Co., Ltd. (Huzhou, China), respectively. Tannic acid (TA), humic acid (HA) and sodium dodecyl benzene sulfonate (SDBS) were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Other chemicals in this work were of analytical reagent acquired from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). STWW samples with a high NO$_3^-$-N concentration were obtained from a local municipal wastewater treatment plant in Nanjing, China.

2.2. Preparation and Characterization of AEE-3

D311 resin was firstly rinsed successively with 1 mol/L HCl and 1 mol/L NaOH in turn to remove impurities, and then washed with deionized water until neutral. Finally, resin was washed by ethyl alcohol and then dried at 323 K for 8 h.

The synthesis method of AEE-3 is the following (Scheme 1): 10 g of dried D311 resin was swelled in 100 mL of acetonitrile for 2 h. Afterwards, 20 mmol of KI and 20 mmol C$_3$H$_7$Br were added separately and the mixture maintained with stirring at 333 K for 48 h. After alkylation, the obtained resin beads were rinsed successively with dilute HCl, distilled water and dilute NaOH to attain a neutral pH. Finally, the product was extracted with anhydrous ethanol and dried at 323 K for 8 h. The obtained resin AEE-3 was characterized by Fourier transform infrared spectrometer (Nicolet 5700, Madison, USA) and N$_2$ adsorption analysis (ASAP-2010C, Micromeritics, Norcross, GA, USA).
2.4. Column Adsorption and Desorption

The adsorption-desorption isotherms and the pore size distribution curve of D311 and AEE-3 are displayed in Figure 1. The isotherm plot of two resins can be considered type IV with a hysteresis loop in the relative pressure range of 0.8–1.0, hinting at the existence of both mesopores and macropores in these resins. Table 1 lists the essential properties of D311 and AEE-3.

The FT-IR spectra of D311 and AEE-3 samples are shown in Figure 2. Notably, two bands with peaks at 1366 cm\(^{-1}\) and 2930 cm\(^{-1}\) are ascribed to asymmetric bands of the alkyl groups (\(-\text{CH}_2-\)and-\text{CH}_3\)), and the peak at 1478 cm\(^{-1}\) is assigned to C–N group. The appearance of a new band at 1407 cm\(^{-1}\) is assigned to C–N group. The appearance of a new band at 1407 cm\(^{-1}\) indicates the alkylation reaction of C\(_3\)H\(_7\)Br onto D311 resin.

3. Results and Discussion

3.1. Characterization

The adsorption-desorption isotherms and the pore size distribution curve of D311 and AEE-3 are displayed in Figure 1. The isotherm plot of two resins can be considered type IV with a hysteresis loop in the relative pressure range of 0.8–1.0, hinting at the existence of both mesopores and macropores in these resins. Table 1 lists the essential properties of D311 and AEE-3.

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is associated with $–\text{CH}_2–\text{CH}_2–N^+\text{R}_3$ group [7]. On the other side, the fact that the strong base ion-exchange capacity of the resin increased from 0 to 3.42 mmol/g implied that propyl groups were successfully introduced onto the primary amine after alkylation. These observations proved AEE-3 had been synthesized successfully.

**Figure 1.** Nitrogen adsorption–desorption isotherms of D311 (a) and AEE-3 (b) with inset showing the corresponding pore size distribution.
Table 1. Physicochemical properties of two resins.

| Resin   | Strong Base Ion-Exchange Capacity (mmol/g Dry Resin) | Average Pore Diameter a (nm) | BET Surface Area (m²/g) | Pore Volume (cm³/g) |
|---------|------------------------------------------------------|-------------------------------|-------------------------|---------------------|
| D311    | 0                                                    | 40.92                         | 31.88                   | 0.36                |
| AEE-3   | 3.42                                                 | 47.44                         | 23.46                   | 0.20                |

*a BJH Desorption average pore diameter.

3.2. Adsorption Kinetics

Figure 3 describes the effect of contact time on NO₃⁻-N uptake by AEE-3 and A520E at 298 K, and all the data were simulated using two commonly used kinetic models [21,22]:

Pseudo – first – order : \[ Q_t = Q_e (1 - e^{-k_1 t}) \] (3)

Pseudo – second – order : \[ Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \] (4)

The initial adsorption rate was calculated by Equation (5):

\[ h_0 = k_2 Q_e^2 \] (5)

where \( Q_e \) (mg/g) is the equilibrium adsorption capacity of NO₃⁻-N, and \( Q_t \) (mg/g) refers to the amounts of NO₃⁻-N in resins at time \( t \) (min). \( k_1 \) (1/min) and \( k_2 \) (g/(mg·min)) represent the rate constants for the pseudo-first- and pseudo-second-order kinetic models, respectively. \( h_0 \) is the initial adsorption rate (mg/(g·min)). The kinetic parameters, together with the coefficient of determination (\( R^2 \)), are listed in Table 2. It is evident that the adsorption behavior of NO₃⁻-N onto both resins was preferable to fit the pseudo-second-order based on the \( R^2 \) values. Obviously, AEE-3 exhibited a greater capacity for NO₃⁻-N than A520E, illustrating that the introduction of alkyl chains would form quaternary ammonium groups which can easily interact with NO₃⁻-N via electrostatic attraction. Finally, a larger \( h_0 \) value of AEE-3 was obtained, and the difference in the adsorption rate is related to the difference of the resin matrix.
Figure 3. Adsorption kinetics of NO$_3^-$-N onto two resins at 298 K.

Table 2. Kinetic parameters of NO$_3^-$-N adsorption by two resins.

| Resin   | $Q_{e,exp}$ (mg/g) | Pseudo-First-Order | Pseudo-Second-Order |
|---------|--------------------|--------------------|--------------------|
|         | $Q_e$ (mg/g) | $k_1$ (1/min) | $R^2$ | $Q_e$ (mg/g) | $10^3k_2$ (g/(mg·min)) | $R^2$ | $h_0$ (mg/(g·min)) |
| AEE-3   | 32.75 | 30.85 | 0.327 | 0.9371 | 33.66 | 6.06 | 0.9819 | 7.13 |
| A520E   | 30.22 | 29.19 | 0.100 | 0.9897 | 30.14 | 1.45 | 0.9987 | 1.16 |

3.3. Effect of Coexisting Anions

In general, some coexisting anions in water would strongly compete with NO$_3^-$-N to occupy active sites via electrostatic interaction. Thus, the selective absorption of resin is of vital importance in evaluating the practical application, as well as in considering the absorption performance. A520E is known for its good selectivity toward NO$_3^-$-N, and its adsorption capacities are still relatively high in the presence of Cl$^-$ or SO$_4^{2-}$ [20]. As displayed in Figure 4, a slightly higher adsorption amount of AEE-3 was detected compared to A520E with an identical addition of anions. The phenomena may be rationalized by the fact that the long alkyl chain on AEE-3 is conducive to the adsorption selectivity for NO$_3^-$-N with lower hydration energy than Cl$^-$ or SO$_4^{2-}$.
were fitted by both Langmuir and Freundlich equations which are represented as follows [25,26]:

The isotherms of NO$_3^-$-N adsorption by AEE-3 are displayed in Figure 6. The experimental data were fitted by both Langmuir and Freundlich equations which are represented as follows [25,26]:

\[
Q_e = \frac{Q_mKLC_e}{1 + KLC_e} \quad (6)
\]

\[
Q_e = KFC_e^{1/n} \quad (7)
\]

Figure 4. Effect of competitive anions Cl$^-$ and SO$_4^{2-}$ on NO$_3^-$-N removal by two resins.

3.4. Effect of pH

The primary mechanism for NO$_3^-$-N uptake onto a strongly basic anion exchanger can be explained by electrostatic interaction or columbic force [23]. Figure 5 displays the influence of solution pH varying from 4.0 and 10.0; the adsorption capacity of NO$_3^-$-N on AEE-3 was in the range of 25.5 to 26.0 mg/g under a Cl$^-$ concentration of 200 mg/L. It shows a considerable amount of NO$_3^-$-N uptake independent of the pH for the strongly basic anion exchanger. It may be concluded that the quaternary tripropylamine groups of AEE-3 could remain stable, thereby causing steady adsorption activity for NO$_3^-$-N under both acidic and alkaline conditions [24].

Figure 5. Effect of pH on NO$_3^-$-N removal by AEE-3.

3.5. Adsorption Isotherms

The isotherms of NO$_3^-$-N adsorption by AEE-3 are displayed in Figure 6. The experimental data were fitted by both Langmuir and Freundlich equations which are represented as follows [25,26]:

\[
Q_e = \frac{Q_mC_e}{1 + KLC_e} \quad (6)
\]

\[
Q_e = KFC_e^{1/n} \quad (7)
\]
where $C_e$ (mg/L) is the concentration at equilibrium state, $Q_e$ (mg/g) is the adsorption capacity at equilibrium state, $Q_m$ (mg/g) is the maximum adsorption capacity, $K_L$ is the Langmuir constant and $K_F$ and $n$ are the Freundlich constants. The $R^2$ of the isothermal fit are presented in Table 3.

In view of the $R^2$ values, the equilibrium adsorption of NO$_3^-$-N onto AEE-3 was better described by the Langmuir isotherm, which coincided with the prevalent ion-exchange mechanism [7,23]. Moreover, the $Q_m$ values of AEE-3 dropped with the increase of temperature, revealing that the NO$_3^-$-N adsorption by the resin was an exothermic process, and therefore, reducing the temperature benefited NO$_3^-$-N uptake.

The maximum NO$_3^-$-N adsorption amount of AEE-3, as evaluated according to the Langmuir model, was compared with other materials including chitosan, activated carbon and commercial anion exchange resins (A520E and D201), etc. As shown in Table 4, the $Q_m$ of AEE-3 for NO$_3^-$-N uptake was higher than that of these commercially available materials, signifying that the novel anion exchange resin can act as a potential material for the technological application of NO$_3^-$-N removal from water.

![Equilibrium isotherm for NO$_3^-$-N adsorbed using AEE-3.](image)

**Figure 6.** Equilibrium isotherm for NO$_3^-$-N adsorbed using AEE-3.

**Table 3.** Isotherm parameters for NO$_3^-$-N adsorption at 288, 303, and 318 K.

| T (K) | Langmuir Model | Freundlich Model |
|-------|----------------|-----------------|
|       | $K_L$ | $Q_m$ (mg/g) | $R^2$ | $K_F$ | $n$ | $R^2$ |
| 288   | 0.12  | 40.32          | 0.9915 | 7.18  | 2.21 | 0.9816 |
| 303   | 0.10  | 40.00          | 0.9977 | 6.39  | 2.13 | 0.9810 |
| 318   | 0.09  | 39.45          | 0.9973 | 5.66  | 2.06 | 0.9721 |

**Table 4.** Comparison of NO$_3^-$-N maximum adsorption capacity ($Q_m$) by different materials.

| Samples                                                                 | $Q_m$ (mg/g) | Reference |
|-------------------------------------------------------------------------|--------------|-----------|
| Chitosan/PVA                                                             | 35.00        | [27]      |
| Cationic polymer-modified granular activated carbon (CPMG)               | 27.56        | [28]      |
| Modified commercial activated carbon                                    | 21.51        | [29]      |
| Magnetic anion-exchange resin MD217                                     | 30.40        | [30]      |
| A520E                                                                    | 36.15        | [31]      |
| D201                                                                     | 38.46        | [31]      |
| AEE-3                                                                    | 40.32        | This study |
3.6. Effect of DOMs on Static Adsorption and Desorption

Figure 7 shows the adsorption amounts of NO$_3^-$-N using AEE-3 and A520E in a bi-solute system (HA/NO$_3^-$, SDBS/NO$_3^-$ or TA/NO$_3^-$) for four adsorption-desorption cycles. It was seen that the adsorption capacities of A520E for NO$_3^-$-N distinctly declined over the four cycles. DOMs can occupy more active sites through hydrophobic and electrostatic interactions on the A520E resin with a polystyrene matrix [12]. By contrast, AEE-3 exhibited greater NO$_3^-$-N adsorption in bi-solute systems, and the reduction of NO$_3^-$-N uptake was slight with increasing the number of adsorption-desorption cycles. This result validated the hypothesis that AEE-3 has a strong resistance to interferential organics due to its hydrophilic matrix. Besides, over 94% of the adsorbed NO$_3^-$-N on AEE-3 was desorbed, while the desorption rates of A520E in the presence of organic matters declined gradually with the number of adsorption-desorption cycle (Figure 8). In addition, Figure 9 presents the desorption rates of DOMs regenerated by a NaCl solution, and the low values for A520E resin can be attributed to the strong affinity between the polystyrene matrix and the hydrophobic organics, causing the DOMs to not be removed fully by regeneration. Hence, these results demonstrate an improved performance on adsorption/regeneration of AEE-3 compared to A520E.

![Figure 7. Effect of different DOMs (HA, TA or SDBS) on NO$_3^-$-N removal by AEE-3 and A520E.](image-url)
3.7. Effect of DOMs on Column Mode Experiments

It is imperative to test the utilization efficiency of adsorbents in a dynamic fixed-bed experiment related to real operating systems [32]. The influence of three organics on NO$_3^-$-N adsorption was studied using an influent with constant NO$_3^-$-N concentration of 20 mg/L in the presence of HA, TA and SDBS. As can be seen in Figure 10, the breakthrough curves (Run 2 and Run 3) for NO$_3^-$-N adsorption onto AEE-3 have a close coincidence with the original breakthrough curve (Run 1). Nevertheless, a large separation between the three breakthrough curves was observed for NO$_3^-$-N adsorption onto A520E, which is indicative of a limited reusability of A520E towards NO$_3^-$-N solution containing DOMs.
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3.8. Assessments of Practical Application

Conventional heterotrophic denitrification techniques are severely restricted by the low C/N ratio of wastewater, thereby causing the high NO$_3^-$-N content in STWW [33,34]. To further assess the practical application of AEE-3, the dynamic column test of NO$_3^-$-N uptake onto AEE-3 was performed using a real STWW effluent which was collected from a local sewage treatment plant, containing the following quality parameters: pH, 6.54; NO$_3^-$-N, 20 mg/L; COD, 39 mg/L; TDS, 436 mg/L. The breakthrough curves of AEE-3 are shown in Figure 11. An inconspicuous deviation between Run 1 and Run 3 breakthrough curves was found, further confirming its potential application in the removal of NO$_3^-$-N from real STWW effluent.
Figure 11. Breakthrough curves of NO$_3^-$-N adsorbed on AEE-3 in real STWW.

4. Conclusions

The strong base polyacrylic AER AEE-3 could be developed and utilized to absorb NO$_3^-$-N selectively from aqueous solutions. Batch adsorption studies exhibited that a pseudo-second-order model was appropriate for depicting the kinetic process, and that the best fit for the isotherms data was Langmuir model. In addition, AEE-3 displayed a greater adsorption capacity and better regeneration capability for NO$_3^-$-N uptake than the commonly-used, nitrate-selective AER A520E in the presence of interferential DOMs. Notably, the effective adsorption of NO$_3^-$-N in real STWW by AEE-3 packed in fixed-bed columns revealed its promising potential in the removal of NO$_3^-$-N from actual complex wastewater.

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