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Characterization and evaluation of a macroporous anion exchange resin for nitrate removal from drinking water

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ABSTRACT

The traditional drinking water purification process is inefficient in removing nitrate significantly. Ion exchange may be the most practical method for the removal of nitrate from drinking water. In this study, an anion exchange resin (PBE-8) was synthesized for selective nitrate removal. The PBE-8 resin was characterized by Fourier transform infrared spectrometry, scanning electron microscopy, and BET surface area analyses. Batch adsorption experiments were carried out to evaluate the thermodynamic and kinetic behaviors of the PBE-8 resin for the adsorption of nitrate. The results indicated that the maximum equilibrium nitrate uptake of PBE-8 was 26.19 mg N/g, which was higher than that of Purolite A 520E (23.07 mg N/g), but lower than that of HZ-222 (33.57 mg N/g). PBE-8 and Purolite A 520E demonstrated better adsorption of nitrate than HZ-222 in the presence of competing anions, such as sulfate, chloride, and bicarbonate in aqueous solution. The Gibbs free energy change (−12.15 to −1.15 kJ/mol), enthalpy change (0.35–7.73 kJ/mol), and entropy change (0.005–0.066 kJ/mol K) indicated that the adsorption of aqueous nitrate by PBE-8 was feasible, endothermic, and spontaneous. Furthermore, the nitrate adsorption by the PBE-8 resin showed a better fit to the Langmuir isotherm and pseudo-second-order kinetic models. Intraparticle diffusion was the main rate-limiting step.

Keywords: Nitrate removal; Drinking water; Anion exchange resin; Adsorption; Rate-limiting step

1. Introduction

Nitrate pollution in waterways, including groundwater and surface water, has significantly increased across the world [1,2]. This trend has raised major concerns due to the ability of nitrates to cause methemoglobinemia in infants and human gastric cancer [3–5]. The concentrations of nitrate in groundwater usually reach 40–50 mg/L in France, Russia, Netherlands, and America, and are even as high as 500–700 mg/L in other places [6–8]. According to investigations at 641 sites in 8 provinces in northern China, 73.8% of the groundwater could not be used as a source for drinking water production in 2009, since the main pollutants included nitrate [9]. As a

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dissolved salt, nitrate cannot be removed effectively during the traditional drinking water purification process, i.e. coagulation, flocculation, sedimentation, and filtration, which mainly aims at removing colloids [10]. Therefore, the search for alternative methods for efficient removal of nitrate from water has raised public concerns worldwide.

The treatment methods currently available for nitrate removal include biological denitrification, chemical reduction, reverse osmosis, electrodialysis, and ion exchange [3]. Biological denitrification is not sufficient to treat low nitrate-polluted water, especially under the condition of carbon source shortage. Additionally, there are some limitations due to the contamination of drinking water with germs and metabolic substances. Chemical reduction, reverse osmosis and electrodialysis are not commonly used because of their high costs. Thus, the ion-exchange process seems to be the most suitable method for drinking water purification and for the removal of inorganic ions owing to its simplicity, effectiveness, relatively low cost, and chemical stability [11]. Therefore, research on novel adsorbents based on the ion-exchange technology is attracting global interest in terms of its practical application. Some common anions, such as sulfate, bicarbonate, and chloride widely exist in natural water sources. Their existence can strongly interfere with the adsorption of nitrate to active sites during the process of nitrate removal, which would result in less removal of nitrate and excessive regeneration of adsorbents. Therefore, studies on the selective absorption of nitrate in the presence of competing anions are becoming increasingly necessary to enhance nitrate removal from drinking water.

Chloromethylated poly(styrene-divinylbenzene) particle is an important precursor of many functional polymer particles, which can be used to prepare nitrate selective ion-exchange resins. The traditional chloromethylation approach for poly(styrene-divinylbenzene) particles mainly includes two methods. One is the reaction of poly(styrene-divinylbenzene) particles with chloromethyl ether or bis-chloromethyl ether in the presence of a Lewis acid. The other method is the copolymerization of p-chloromethyl styrene, styrene, and divinylbenzene. However, chloromethyl ether and bis-chloromethyl ether have significant carcinogenic effects on the human body, especially the lungs. Consequently, this method has been limited for a long time all over the world. The second method suffers from the high cost of p-chloromethyl styrene [12], which make large-scale preparation of chloromethylated poly(styrene-divinylbenzene) particles (CPSM) with p-chloromethyl styrene unattractive. Therefore, much attention should be paid to the new chloromethylation method of poly(styrene-divinylbenzene) particles.

In this study, a macroporous nitrate selective exchange resin, PBE-8, was formulated via polymerization, chloromethylation by 1,4-bis(chloromethoxy) butane, followed by quaternarization. The physicochemical properties of the resin were characterized, and the equilibrium and kinetic parameters for nitrate adsorption from aqueous solution were investigated. Also, the effects of competing anions on nitrate removal were evaluated.

2. Materials and methods

2.1. Materials

The monomers to be polymerized were styrene (ST, 99%) and divinylbenzene (DVB, containing 80% DVB isomers, the remainder mainly being 3- and 4-ethylvinylbenzene). Styrene was supplied by Kermel Chemical Reagent Co., Ltd (Tianjin, China) and DVB was provided by Jingchun Scientifical Co., Ltd (Shanghai, China). Prior to polymerization, both monomers were pre-treated to remove the inhibitor, 4-tert-butylcatechol (TBC). The initiator, benzoyl peroxide (BPO, 99%, remainder water), was supplied by Fuchen Chemical Reagent Co., Ltd (Tianjin, China). 1,4-bis(chloromethoxy) butane (BCMB, 99%) was supplied by Langene bio-science Co., Ltd (Xi’an, China) and used as the chloromethylation reagent. The catalyst for the chloromethylation reaction, anhydrous stannic chloride was provided by Sinopharm chemical reagent company (China). Two strong nitrate selective anion exchange resins, Purolite A 520E (A 520E) and HZ-222 were chosen for comparative experiments and were, respectively, provided by Purolite Int. Ltd, England, and Hebei Huazhong Chemical Co., Ltd, China. All other reagents were of analytical grade and obtained from Kermel Chemical Reagent Co., Ltd, and used without further purification. Deionized water was used to prepare the aqueous solutions.

2.2. Methods

The macroporous strong basic anion exchange resin named as PBE-8 was prepared via three-stage reactions, which consist of suspension polymerization [13], chloromethylation, and quaternarization. The details of the process are described below: a 2 L glass reaction kettle equipped with a thermometer, a reflux condenser, and a mechanical stirrer was charged with 725.8 mL (2.5%) polyvinyl alcohol and 181.4 mL (2%) gelatine solution. The mixture was heated to 60℃. Meanwhile, 240 mL of ST, 12 mL of DVB, 201.6 mL of liquid paraffin, and 2.27 g of BPO were mixed and then added to the former solution. Subsequently, the glass reaction kettle was heated at 95–100℃ with continuous stirring at 170 rpm for 10 h. The poly(styrene-divinylbenzene) particles (PSM) were obtained by filtration and were extracted with ethanol for 8 h in a Soxhlet apparatus. Next, 20 g of PSM was first swollen in the mixture of dichloromethane (200 mL) and BCMB (36 g) for at least 1 h. Then, 20 mL of anhydrous stannic chloride was added. The reactant mixture was stirred at 150 rpm for 6 h at room temperature. Subsequently, the CPSM was filtered and washed with dilute hydrochloric acid, 1,4-dioxane, distilled water and alcohol, respectively. Finally, PBE-8 resin was obtained by the quaternarization of CPSM (20 g) with triethylamine (30 mL) in deionized water (100 mL) at 60℃ for 24 h.

Batch adsorption experiments at 25℃ were carried out in 150-mL conical flasks by adding a specified amount of the resin in contact with 50 mL of nitrate solution. The solutions were placed in flasks and after the addition of the resin, shaken at a constant speed of 150 rpm for 24 h in an oscillating incubator (BS-2F, Jintan, China). The details of the batch experimental procedure were described by Milmile and Samatya [3,14]. The adsorption kinetics study was carried out with a fixed resin dose of 0.15 g resin/50 mL of solution. The initial nitrate concentration was 100 mg N/L. The nitrate concentration was subsequently measured at predetermined time intervals of 0–160 min.

The adsorption isotherm study was carried out at a fixed resin dose of 0.15 g resin/50 mL of solution using different initial nitrate concentrations (5, 10, 15, 20, 40, 60, 80, 100, 150, and 200 mg N/L). All other parameters were kept constant. In order to determine the optimum amount of the resin for nitrate removal from aqueous solution, the dose of resin was varied at 0.01, 0.02, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, and 0.8 g resin/50 mL of solution with the initial nitrate concentration of 100 mg N/L. The effect of temperature on nitrate removal was evaluated at a fixed resin dose of 0.15 g resin/50 mL of solution and initial nitrate concentration of 100 mg N/L. The effects of increased competing anions (Cl^-, HCO_3^-, and SO_4^{2-}) on nitrate retention of the three resins were investigated by keeping the concentration of nitrate (100 mg N/L) constant, and the dose of resin was fixed at 0.15 g/50 mL of solution.

Studies on the column adsorption performance were carried out using a glass column with an inner diameter of 2.2 cm at room temperature. PBE-8 resin of 36.8 g was packed into the glass column at 38 cm. The nitrate solution with an initial concentration of 50 mg N/L was continuously passed through the column at a flow rate of 27 mL/min. Samples were collected at the bottom of the column at regular intervals.

The amounts of nitrate adsorbed at equilibrium (Q_e, mg/g) were calculated by Eq. (1) [3].

$$Q_e = \frac{V(C_0 - C_e)}{W} \tag{1}$$

The experimental results of the nitrate adsorption isotherms were fitted to the Langmuir (Eq. (2)), Freundlich (Eq. (3)), and D–R adsorption (Eq. (4)) isotherm models [3,15].

$$Q_e = \frac{Q_0 b C_e}{1 + bC_e}, \quad r = \frac{1}{1 + bC_0} \tag{2}$$

$$Q_e = K_f C_e^{(1/n)} \tag{3}$$

$$\ln Q_e = \ln Q_0 - \beta' \varepsilon^2, \quad \varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right), \quad E = \frac{1}{(-2\beta')^{1/2}} \tag{4}$$

Kinetic data for the three adsorbents were then represented by the pseudo-first-order model (Eq. (5)), the pseudo-second-order model (Eq. (6)), and the Elovich model (Eq. (7)) [16,17].

$$\ln \frac{Q_e - Q_t}{Q_e} = -K_1 t + A \tag{5}$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e}, \quad h = K_2 Q_e^2 \tag{6}$$

$$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{7}$$

2.3. Characterization

The surface physical morphology of the PBE-8 resin was observed using a scanning electron microscope (SEM) (JEOL, JSM-6510LV, Japan). The surface functional groups of PSM, CPSM, PBE-8, A 520E, and HZ-222 were detected by a Fourier transform infrared (FT-IR) spectrometer (Bruker Optik GmbH, VERTEX 70v, Germany), where the spectra were recorded in the wave number ranging from 400 to 4,000 cm^{-1}. N_2 adsorption–desorption tests were carried out at 77.35 K to determine the specific surface area and pore size distribution based on the BJH model using an automated surface area and pore size analyzer NOVA 4200e (Quantachrome Instruments corporate, US). Nitrate-nitrogen was analyzed using a UV spectrophotometer (STECH, 752 N, China) at a wavelength of 220 nm. One milliliter of 1.0 mol/L HCl and 0.1 mL of 0.8 wt.% sulfamic acid were added to 50 mL of the sample in order to eliminate the interface of organic ions and nitrite, respectively.

3. Results and discussion

3.1. Characterization of PBE-8 resin

Fig. 1 were the SEM images of PBE-8 resin magnified for 50 times (a), 2,000 times (b), and 10,000 times (c), which indicated that the synthesized resin consisted of spherical particles with uniformly distributed holes. The structural changes of PSM, CPSM, PBE-8, A 520E, and HZ-222 were investigated by FT-IR. The absorption peaks marked as PSM (Fig. 2(a)) were the qualitative characteristic absorption peaks of the styrene-divinylbenzene copolymer. The peak at 1,600 cm^{-1} belongs to aromatic ring. By comparing with PSM, the three strong characteristic bands at 670 cm^{-1}, 1,421, and 1,265 cm^{-1} were due to C–Cl stretching vibrations, C–H flexural vibrations of chloromethyl groups ($–CH_2Cl$), and C–H flexural vibrations of the benzene ring in CPSM, respectively. Furthermore, the characteristic absorption peak of disubstituted benzene at 828 cm^{-1} was significantly strengthened. Three new absorption bands at 1,016, 1,452, and 1,380 cm^{-1}, corresponding to C–N stretching vibrations, C–H flexural vibrations of methylene, and C–H flexural vibrations of methyl of $–CH_2–N^+(CH_2CH_3)_3$ groups were observed. The peak at 670 cm^{-1} was weakened, but it did not disappear entirely. Therefore, it could be inferred that the chemical structure of the PBE-8 resin might be as shown in Fig. 2(a). These results strongly demonstrated that the PBE-8 resin had been synthesized successfully. The probable chemical structures of A 520E and HZ-222 are as shown in Fig. 2(b), which were derived from the analysis of the three FT-IR spectra curves and the physicochemical properties of A 520E and HZ-222 (Table 1).

3.2. Effect of resin dosage, temperature, and pH on nitrate adsorption

Fig. 3(a) depicts the nitrate removal as a function of resin dosage, which shows that the nitrate removal increases with an increase in the resin dosage. The optimum amounts of A 520E, HZ-222, and PBE-8 resins were 0.3 g resin/50 mL of nitrate solution. The highest removal rate was recorded for PBE-8, which could reach 99.81% at the resin dosage of 0.7 g,

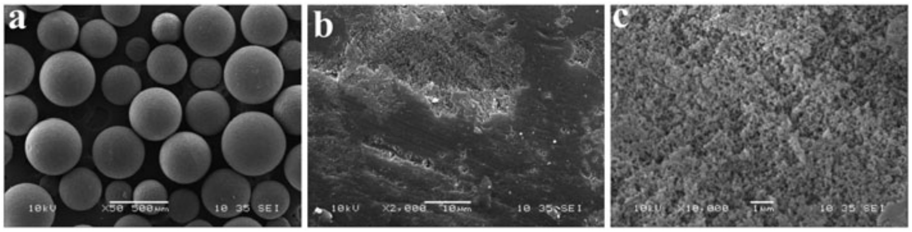

Fig. 1. SEM images of the PBE-8 resin at magnification of (a) ×50, (b) ×2,000, and (c) ×10,000.

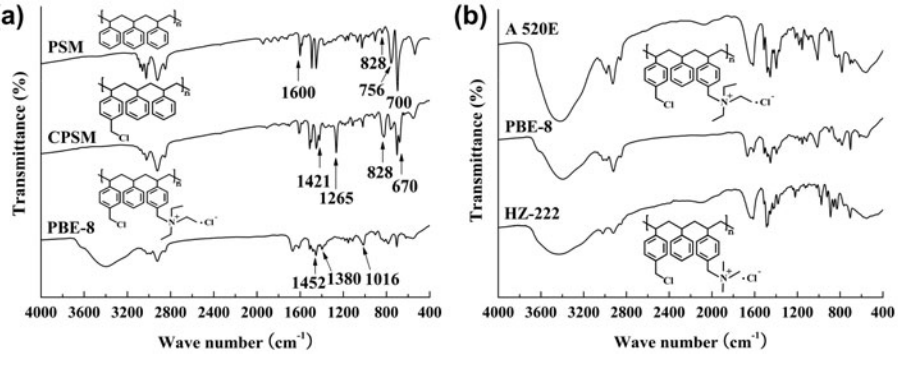

Fig. 2. FT-IR spectra of PSM (a), CPSM (a), PBE-8 (a and b), A 520E (b), and HZ-222 (b).

Table 1
Physicochemical properties of the resins (dry)

Property	A 520E	HZ-222	PBE-8
Skeleton	Macroporous ST-DVB	Macroporous ST-DVB	Macroporous ST-DVB
Physical aspect	Opaque cream spherical beads	Opaque cream spherical beads	Opaque cream spherical beads
Functional groups	$R(CH_2CH_3)_3\ N^+$ [18]	$R(CH_3)_3\ N^+$	$R(CH_2CH_3)_3\ N^+$
Ionic form	Cl^-	Cl^-	Cl^-
Granulometry (mm)	0.3–1.3	0.3–1.3	0.3–1.3
BET surface area (m^2/g)	10.4	2.6	11.2
Micropore area (m^2/g)	0.96	0.15	0.92
Average pore diameter (nm)	16.4	5.2	18.3
Pore volume (mL/g)	0.04	0.003	0.05

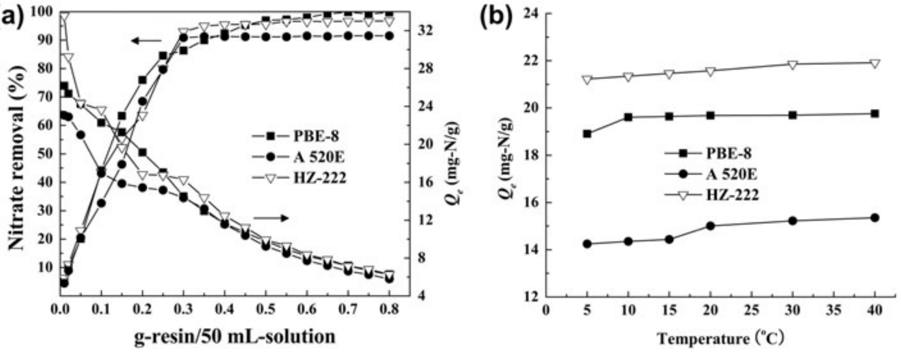

Fig. 3. Effect of resin dosage (a) and temperature (b) on nitrate adsorption.

implying that PBE-8 resin was more suitable for the treatment of low nitrate-polluted water than A 520E and HZ-222. Gradual increases in nitrate adsorption by the three resins were observed with the increase in temperature (Fig. 3(b)). The increase in temperature provided a driving force to overcome the mass transfer resistance between the resin/solution interfaces. The increase in nitrate adsorption by the PBE-8 resin demonstrated the endothermic nature of the adsorption. The pH value of the nitrate solution was adjusted with 1 mol/L of HCl or NaOH. The amounts of nitrate adsorbed by the PBE-8 resin at the pH of 2, 5, 7, 9, and 11 varied at 17.33, 18.74, 19.42, 17.60, and 17.21 mg N/g, respectively, indicating that a neutral pH condition was more favorable for the nitrate adsorption. This phenomenon was probably due to the presence of excess hydroxyl ions at higher pH and chloride ions at lower pH, which would compete with the nitrate for adsorption sites on the PBE-8 resin, resulting in a decreased adsorption of nitrate.

3.3. Effect of competing anions on nitrate adsorption

The effects of increased competing anions (Cl^-, HCO_3^-, and SO_4^{2-}) on nitrate retention by the three resins were investigated by keeping the concentration of nitrate constant. As shown in Fig. 4, bicarbonate had the lowest impact on the removal of nitrate compared to chloride and sulfate. The selectivity of nitrate removal by PBE-8 and A 520E was better than that of HZ-222 due to the presence of triethylamine exchange sites [18], and their similar skeleton structure (Fig. 2(b), Table 1). Besides, PBE-8 showed a higher adsorption capacity for nitrate than A 520E. The results (Fig. 4) suggested that the affinity sequence was $NO_3^- > SO_4^{2-} > Cl^- > HCO_3^-$.

The adsorption mechanism of anions by adsorbents is mainly dependent on the physicochemical properties of the anions and their interaction with the adsorbent surface. The physicochemical properties of anions, such as ionic radius, hydrated radius, hydration energy, and bulk diffusion coefficient are crucial for their selective adsorption [19]. Some of the important characteristics of the inorganic anions involved are summarized in Table 2. In aqueous environments, the apparent ionic size is determined by the hydrated radius rather than the ionic radius [20]. The hydrated radius does not appear to be a significant factor for the selectivity of PBE-8 and A 520E due to their large pore sizes (See Table 1) and small hydrated radius of

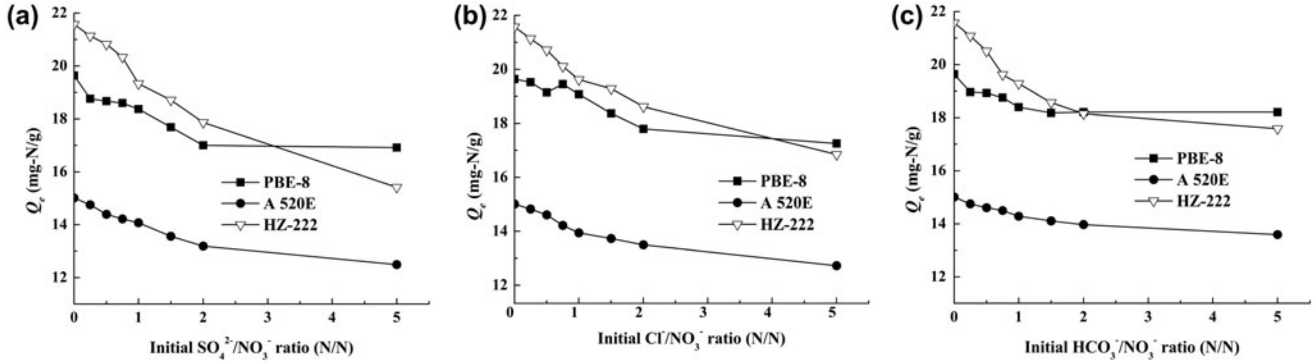

Fig. 4. Effect of sulfate (a), chloride (b), and bicarbonate (c) on nitrate adsorption.

anions (Table 2). Therefore, hydration free energy may play a more significant role in the adsorption selectivity of the resin for anions. It is well known that the variations in the chain length at the active sites from the trimethyl to triethyl could result in an increase in the hydrophobicity of the resin, and thus, be more selective in adsorbing anions with lower hydration energies [21,22]. The hydration energy of nitrate is lower than those of Cl^- and SO_4^{2-} (Table 2). Consequently, it is understandable that the PBE-8 and A 520E resins preferentially adsorb nitrate, and that PBE-8 resin could be utilized as an effective adsorbent for the selective removal of nitrate in the presence of competing anions.

3.4. Equilibrium adsorption isotherm studies

Table 3 shows that the behavior of the nitrate adsorption by PBE-8 resin and A 520E can be better represented by the Langmuir isotherm than Freundlich and D–R isotherms, having recorded a higher regression coefficient. However, the Freundlich adsorption isotherm model was satisfactory for simulating the experimental data of HZ-222 resin. This phenomenon could be attributed to the nitrate adsorption by active sites on the heterogeneous resin surface of the HZ-222 resin, which exhibited multilayer adsorption properties. Furthermore, the values of the separation factor (r) of the Langmuir isotherm and the exponent of the Freundlich isotherm (n) were calculated to estimate the adsorption type. The r-values for A 520E, HZ-222, and PBE-8 were in the range of 0.017–0.406, 0.044–0.649, and 0.020–0.445, respectively. The r-values of the three resins were less than 1, whereas the n-values were larger than 2, which indicated that the processes of nitrate adsorption by the three resins were all favorable. In addition, the n-value of the Freundlich adsorption isotherm of PBE-8 was the lowest among the three chosen resins, indicating that the PBE-8 resin possess the highest capability for nitrate adsorption. For a magnitude of E between 8 and 16 kJ/mol, the adsorption process follows chemical ion exchange while the value of E below 8 kJ/mol indicates physical adsorption [3]. With the value of E (1.158 kJ/mol) as the reference, the process of nitrate adsorption by the PBE-8 resin is related to physical adsorption.

3.5. Thermodynamic studies

Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) are three important

Table 2
Physicochemical properties of different anions

Ion	Chloride	Nitrate	Sulfate	Bicarbonate
Ionic radius (nm)	0.18 [19]	0.3 [19]	0.29 [19]	–
Hydrated radius (nm)	0.38 [19]	0.51 [19]	0.379 [19]	0.2–0.22 [23]
Hydration free energy (kJ/mol)	−347 [19]	−305.85 [19]	−1,090 [19]	–
Bulk diffusion coefficient (10^{-9} m^2/s)	2.03 [19]	1.9 [19]	1.065 [19]	1.185 [23]

Table 3
Isotherm parameters of nitrate adsorption by different adsorbents at 25℃

	Langmuir equation			Freundlich equation			D–R equation		
Adsorbent	Q_0	b	R^2	n	K_f	R^2	Q_0	E (kJ/mol)	R^2
A 520E	20.41	0.293	0.997	3.745	6.339	0.891	17.18	0.741	0.824
HZ-222	28.57	0.108	0.959	4.444	8.670	0.967	18.56	2.840	0.623
PBE-8	21.74	0.249	0.998	2.890	4.920	0.963	16.22	1.158	0.864

parameters used to indicate the thermodynamics of a process. These thermodynamic parameters of the nitrate adsorption process of the PBE-8 resin were calculated according to the method described by Chabani et al. [24] and Turki et al. [15]. The results are presented in Table 4.

With the increase in the initial nitrate concentration, the values of ΔS and ΔH were reduced because of the decrease in ongoing randomness and the heterogeneity of the surface energy of the resin, respectively. The enthalpy change demonstrated that the nitrate adsorption process of PBE-8 was endothermic. The values of ΔG were in the range of −12.15 to −1.21 kJ/mol at initial nitrate concentration ranging from 5 to 100 mg N/L, indicating that the adsorption process was thermodynamically feasible and spontaneous. The decreasing tendency of ΔG with the increase in temperature was noticeable under low initial nitrate concentrations. However, when the initial nitrate concentration was higher than 15 mg N/L, the process became quite insensitive to temperature owing to the concentration driving force.

3.6. Adsorption kinetic studies

As shown in Table 5, the adsorption capacity of the HZ-222 resin was the highest among the three resins. Compared to PBE-8 and HZ-222, A 520E showed the lowest nitrate adsorption capacity. The relatively high correlation coefficients ($R^2 \geq 0.98$) indicated that the adsorption of nitrate by A 520E, HZ-222, and PBE-8 resins could be approximated favorably by the pseudo-second-order model. Moreover, the quantity of nitrate adsorbed by A 520E, HZ-222, and PBE-8, estimated from the pseudo-second-order model were closer to the experimental data.

3.7. Diffusion models and rate controlling step

The kinetics of an exchange resin is typically limited by the following steps: film diffusion control and intraparticle diffusion control. In batch adsorption processes, the rate process usually depends upon $t^{1/2}$ rather than t itself [3,25], which can be expressed using Weber–Morris model [26]:

$$F_{\mathrm{ad}} = \frac{Q_t}{Q_{\mathrm{e}}} = \frac{C_0 - C_t}{C_0 - C_{\mathrm{e}}} = k_{\mathrm{wm}} t^{1/2} \tag{8}$$

Assuming that all the resin particles were of uniform spheres, a variant Boyd model (Eq. (9)) could be employed to analyze the diffusion mechanism.

$$F_{\mathrm{ad}} = 1 - \left(\frac{6}{\pi^2}\right) \sum_{m=1}^{\infty} \left[\left(\frac{1}{m^2}\right) \exp(-m^2 B_{\mathrm{b}} t)\right] \tag{9}$$

Table 4
Thermodynamic parameters of nitrate adsorption by the PBE-8 resin

	ΔG (kJ/mol)			
Initial nitrate concentration (mg N/L)	20℃	30℃	ΔS (kJ/mol K)	ΔH (kJ/mol)
5	−11.49	−12.15	0.066	7.73
10	−6.65	−6.98	0.033	3.11
15	−6.93	−7.22	0.029	1.57
20	−6.04	−6.30	0.026	1.53
40	−3.98	−4.14	0.015	0.56
60	−2.67	−2.79	0.012	0.83
80	−1.43	−1.49	0.006	0.42
100	−1.15	−1.21	0.005	0.35

Table 5
Kinetic parameters of nitrate adsorption by different adsorbents at 25℃

	Pseudo-first-order equation			Pseudo-second-order equation			Elovich equation		
Adsorbent	K_1	Q_e	R^2	K_2	Q_e	R^2	α	β	R^2
A 520E	0.034	15.1	0.707	0.025	15.38	0.999	27.883	0.461	0.880
HZ-222	0.024	21.65	0.299	0.053	21.74	0.999	382.985	0.436	0.710
PBE-8	0.038	19.9	0.681	0.014	20.41	0.998	27.334	0.336	0.920

If *F*-value is higher than 0.85, then Eq. (9) can be reduced to:

$$F_{\mathrm{ad}} = 1 - \left(\frac{6}{\pi^2}\right)\exp(-B_{\mathrm{b}}t) \tag{10}$$

If *F*-value is lower than 0.85, the Eq. (9) equals:

$$B_{\mathrm{b}}t = 2\pi - \frac{\pi^2 F_{\mathrm{ad}}}{3} - 2\pi\left(1 - \frac{\pi F_{\mathrm{ad}}}{3}\right)^{1/2} \tag{11}$$

The linearity of $B_{\mathrm{b}}t$ (calculated from Eqs. (10) and (11)) vs t was used to distinguish the rate-controlling step. It can be assumed that diffusion within the resin matrix is the rate-limiting step on condition that the plot is a straight line passing through the origin. Otherwise, it would be governed by film diffusion. As shown in Fig. 5, two phases with different slopes and intercepts could be observed. In the first phase, adsorption was linear and characterized by an extremely fast uptake. In the second phase, the adsorption rate became slower. The slope of Fig. 5(b) was abrupt, which could be attributed to the high adsorption capacity of HZ-222 and rapid use of the available active sites on the heterogeneous resin surfaces. Moreover, the straight lines with high regression coefficients (as shown in Fig. 5(d) and (f)) indicated that the adsorption of aqueous nitrates by A 520E and PBE-8

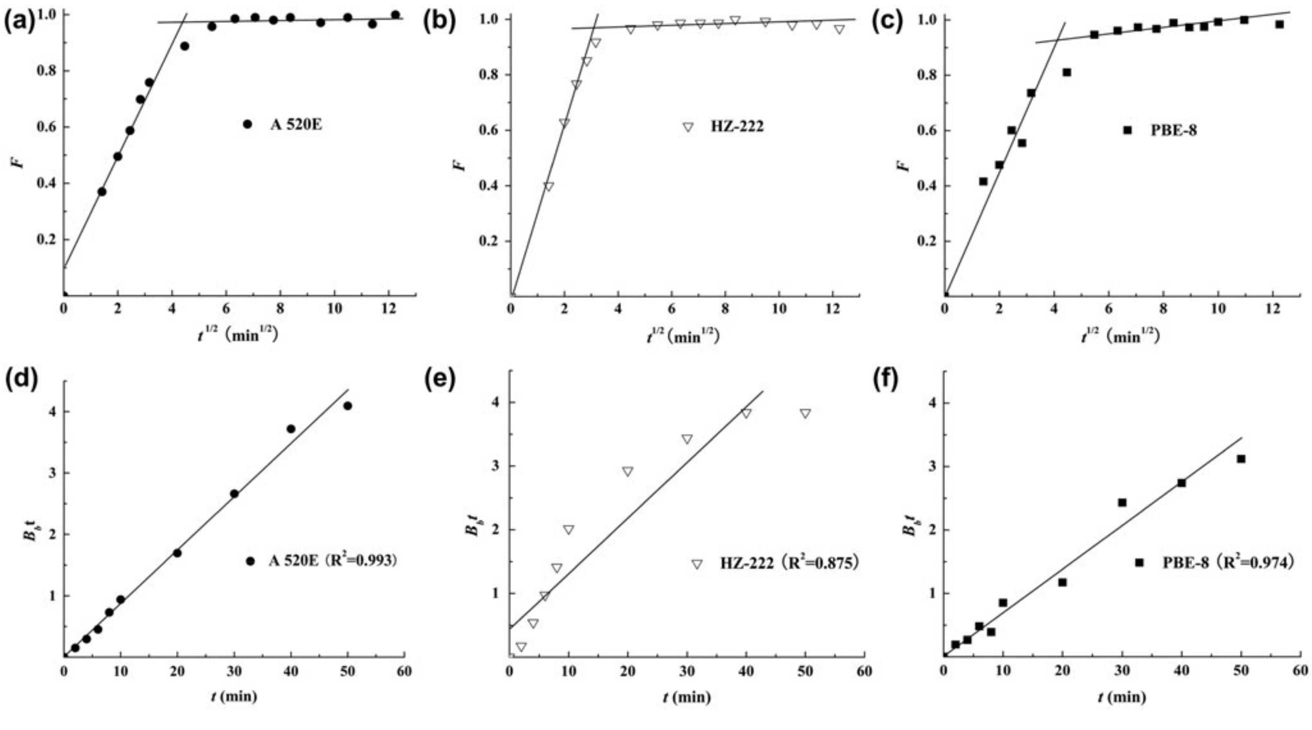

Fig. 5. Effect of $t^{1/2}$ on nitrate adsorption (a, b, and c) and variant Boyd model plots (d, e, and f) of A 520E, HZ-222 and PBE-8.

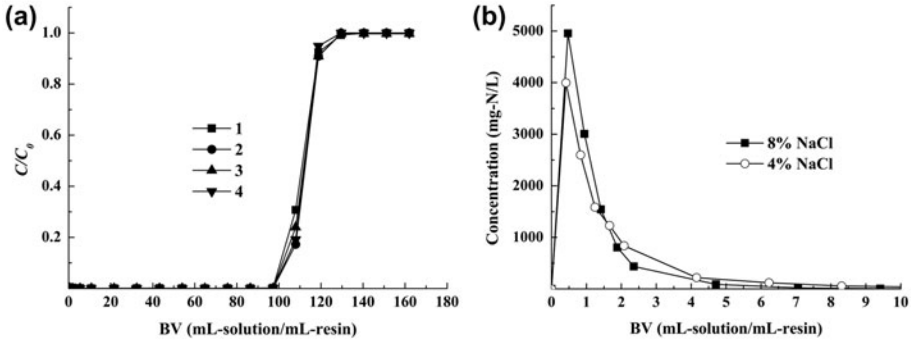

Fig. 6. Breakthrough and elution curves of nitrate obtained by the PBE-8 resin.

were mainly controlled by intraparticle diffusion. However, the straight line of Fig. 5(e) with a lower regression coefficient indicates that the effect of intraparticle diffusion on the adsorption of nitrate by HZ-222 was not significant owing to its hydrophilic chains, which could be the main cause of the low selectivity for nitrate adsorption.

3.8. Column adsorption and regeneration

The column study was performed using a 50 mg N/L model solution. The breakthrough and elution curves of nitrate obtained using the PBE-8 resins are presented in Fig. 6. The nitrate-saturated resin was eluted with 4 and 8 wt.% NaCl solutions. Fig. 6(a) shows that the PBE-8 resin could repeatedly be used. The breakthrough point was 97.2 bed volumes (BV) with a breakthrough capacity of 21.27 mg N/g-resin, using simple nitrate model water. Fig. 6(b) shows the nitrate loaded onto the PBE-8 resin, which was quantitatively eluted with 24.92 BV of 4 wt.% salt solution and 18.83 BV of 8 wt.% salt solution with the corresponding desorption efficiency of 99%. However, the salt consumption of the 8 wt.% salt solution was 1.51 times higher than the 4 wt.% salt solution. Consequently, the 4 wt.% salt solution is considered to be the more efficient liquid for column regeneration.

4. Conclusions

SEM and FT-IR analyses demonstrated that the anion exchange resin, PBE-8 was synthesized successfully. Its maximum adsorption capacity for nitrate was 26.19 mg N/g, which was higher than that of Purolite A 520E (23.07 mg N/g), but lower than that of HZ-222 (33.57 mg N/g). The Langmuir isotherm and pseudo-second-order models described the adsorption of nitrate by the PBE-8 resin reasonably. Selectivity adsorption experiments indicated that the PBE-8 resin has a similar selective adsorption ability for nitrate as A 520E due to the longer alkyl chains on the exchange sites and their similar skeleton structure. Furthermore, the three thermodynamic parameters ΔG, ΔH, and ΔS indicated that the adsorption of nitrate by the PBE-8 resin was feasible, endothermic, and spontaneous under the examined conditions. Intraparticle diffusion was the main rate-limiting step compared with external diffusion and film diffusion. Consequently, the PBE-8 resin with selective adsorption ability toward nitrate could potentially be applied in the purification of polluted drinking water resources.

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Nomenclature

Q_0 — maximum adsorption capacity calculated using Langmuir model (mg/g)
Q_e — amount of adsorption at equilibrium (mg/g)
Q_t — adsorption capacity at time t (mg/g)
C_0 — initial nitrate concentration in the solution (mg/L)
C_e — equilibrium concentration in the solution (mg/L)
C_t — aqueous nitrate concentration at time t in the solution (mg/L)
V — volume of the solution (L)
W — mass of the dry resin (g)
b — Langmuir constants (L/mg)
r — separation factor of Langmuir model
K_f — Freundlich constant ($\mathrm{mg}^{(1-1/n)}\ \mathrm{L}^{1/n}/\mathrm{g}$)
n — Freundlich constants
β' — activity coefficient of D–R model ($\mathrm{mol}^2/\mathrm{J}^2$)

ε — Polanyi potential

E — mean free energy of adsorption (kJ/mol)

K_1 — adsorption rate constant of pseudo-first-order model (1/min)

K_2 — adsorption rate constant of pseudo-second-order model (g/mg min)

α — initial adsorption rates of Elovich model (mg/g min)

β — desorption constant of Elovich model (g/mg)

F_{ad} — saturation factor of adsorption

k_{wm} — constant of Weber–Morris model ($\mathrm{min}^{-0.5}$)

$B_{\mathrm{b}}t$ — overall rate constant

R — universal gas constant (8.314 J/K mol)

T — temperature (K)

t — time (min)

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