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Novel Na-zeolite covalently bonded with quaternary ammonium for simultaneous removal of phosphate, ammonium and nitrate

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ABSTRACT

Phosphate and ammonium, along with nitrate, have been regarded as the main control indicators in the treatment of municipal sewage. However, no promising material has yet been developed for the simultaneous removal of phosphate, ammonium and nitrate. Natural zeolite was modified for the first time by quaternary ammonium group-containing silane coupling agent and sodium chloride. The quaternary ammonium groups were covalently attached to the surface of zeolite. This modified zeolite (QaNaZ) could remove not only phosphate and ammonium but also nitrate from sewage efficiently, with removal efficiency of 94.18%, 48.84%, and 91.11% respectively. The results showed that chemical adsorption was the main mechanism in this spontaneous and endothermic process. The coexisting ions in sewage had no significant effect on the adsorption of QaNaZ. The exhausted QaNaZ could be regenerated easily using dilute sodium chloride solution. QaNaZ would have broad applications in simultaneous removal of nitrogen and phosphate from wastewater.

Keywords: Zeolite; Covalent bonding; Quaternary ammonium; Water treatment; Simultaneous removal

1. Introduction

With the rapid industrialization and urbanization in China, the amount of municipal sewage has increased dramatically in recent years. In 2015, it is estimated that 41.03 billion tons of municipal sewage was discharged in China (China Environmental Status Bulletin, 2015). Municipal sewage after conventional treatment processes would still contain relatively high concentrations of phosphorus and nitrogen mainly existing in the form of inorganic phosphate, ammonium and nitrate. High contents of phosphate and ammonium in municipal water have been of great concern for decades due to their close relationship with eutrophication in the receiving water bodies [1,2]. Besides, water contaminated by nitrate would also have high toxicity and harmful effects on environment and human health [3]. For example, it causes eutrophication in water resources and may cause blue baby syndrome in infants. Owing to the potential threat of nitrate to the receiving environment and human beings, removal of nitrate in water receives much attention recently.

Most municipal sewage treatment plants in China are required to improve water quality of effluent to meet the first level A criteria specified in national effluent standard (GB 18918-2002). According to this standard, the maximum

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permissible levels of P, NH_4^+-N and NO_3^--N in effluent are 0.5 mg/L, 5 mg/L and 10 mg/L respectively [4]. Nevertheless, concentrations of P, NH_4^+-N and NO_3^--N in the tail water after traditional biological treatment in China are still 1 mg/L, 8 mg/L and 15 mg/L approximately. Accordingly, it is essential to further remove phosphate, ammonium and nitrate in secondary effluent of sewage treatment plants. Although biological treatment processes are widely used to reduce concentrations of phosphorus and nitrogen in wastewater [5,6], biological treatment processes could not insure that effluent would meet the strict standards. Moreover, they require more treatment facilities and occupy relatively large area, which is not available in most sewage treatment plants in China. Physical and chemical methods such as coagulation, sedimentation, adsorption and ion exchange have the advantages of high removal capacity, simple operation and less area occupied. However, no promising and cost-effective physicochemical treatment methods are widely available for the simultaneous removal of phosphorus and nitrogen in wastewater yet. Thus, it is desirable to develop an efficient and cost-effective physicochemical treatment technology for the simultaneous removal of phosphate, ammonium and nitrate in a single treatment process.

Natural zeolite (NZ) is a type of porous aluminum silicate mineral, which has desirable physical and chemical properties for ion exchange and adsorption of contaminants. Thus, NZ is extensively used as a cost-effective adsorbent in physicochemical water treatment processes for the removal of ammonium [7,8]. It was reported that the cation exchange capacity (CEC) of zeolite can be greatly improved after impregnated with sodium salt solution [9]. However, NZ cannot efficiently remove the anions in water because of the strong electro negativity exhibited by the silicon (aluminum) oxygen structure [7]. At present, impregnation by metal salt solutions and surfactant modification are widely used to improve the ion exchange capacity of zeolite for anions. For example, calcium, aluminum, iron or lanthanum-modified zeolites have been shown to be excellent candidates for phosphate removal owing to chemical deposition or complexion between metal compounds and phosphate [10–12]. But this type of modified zeolite could not remove nitrate from water efficiently. In addition, cationic surfactants such as hexadecyltrimethy-lammonium bromide (HTAB) and cetylpyridinium bromide (CPB) are also frequently used to modify zeolite to remove oxyanions such as chromate, phosphate and nitrate [13–15]. Charge on the zeolite surface will be reversed from negative to positive when the surfactant concentration exceeds its critical micelle concentration (CMC) and bilayer structure is formed on the external zeolite surface [16]. Although the first layer of adsorbed surfactant molecules is retained on zeolite surface via relatively strong Coulombic interaction, the second layer, which is positively charged and crucial for anion adsorption, is attached to the first layer by weak hydrophobic bonding (van der Waals forces) and forms admicelle [15,17]. Thus, the positive charge on surfactant-modified zeolite is unstable, adversely affecting the performance and regeneration of modified zeolite in removing nitrate. To our knowledge, modified zeolites which have been reported in previous studies [7–12] are not able to effectively remove phosphate, ammonium and nitrate simultaneously.

This study investigated a coupling method to obtain modified zeolite with stable structure and function, which is able to remove phosphate, ammonium and nitrate in wastewater simultaneously. We firstly prepared the zeolite modified with quaternary ammonium group-containing silane coupling agent and sodium chloride, which was subsequently impregnated in sodium chloride solution to obtain the quaternary ammonium-Na-modified zeolite (named QaNaZ), which could remove phosphate, ammonium and nitrate simultaneously. Furthermore, we studied the structure, removal efficiency and adsorption behavior of QaNaZ. The regeneration and performance of regenerated QaNaZ were also investigated in the treatment of sewage.

2. Materials and methods

2.1. QaNaZ preparation

NZ used in this study was obtained from Jiaozhou City of Shandong Province in China. It has the following chemical composition: 60.41% SiO_2 , 33.91% Al_2O_3, 3.18% CaO, 1.48% MgO, 1.02% Na_2O. The NZ samples were firstly washed with deionized water and dried in an oven at 106°C for 2 h and the particles below 350 mesh were used for experiments. The NZ was modified by an adapted method reported by Vassileva [18]. In general, 50 g dried NZ were firstly treated with 20 g 40 wt% quaternary ammonium group-containing silane coupling agent (Dimethyloctadecyl [3-(trimethoxysilyl)propyl] ammonium chloride, $C_{26}H_{58}ClNO_3Si$, Nuokang Chemical Co., Ltd, China) ethanol solution and stirred at 200 rpm for 2 h. The zeolite in the organic form was washed with 1000 mL of alcohol and 2000 mL of deionized water for at least five consecutive times at 200 rpm in the thermostatic shaker (DDHZ-300, TCYQ, China). After dried in an oven at 106°C for 2 h, the zeolite was grinded with mortar and the organic zeolite was obtained. Secondly, 30 g prepared organic zeolite was impregnated in 500 mL NaCl solution (6 wt%) for three consecutive times under vibrating condition for 2 h and then washed with deionized water until no chloride was detected by the $AgNO_3$ test. Finally, after dried in an oven at 106℃ for 2 h, the modified zeolite was grinded again and named as QaNaZ.

2.2. Characterization

Several analytical methods were used to characterize the structures and morphologies of the zeolite samples. The analysis of mineralogical composition of the zeolite samples was conducted by X-ray diffraction (XRD, Shimadzu DMAX-2400, Japan) with mono chromated high intensity Cu $K\alpha_1$ radiation (λ = 0.15406 nm). A FT-IR spectrometer (Thermo Fisher Spectrum 400, USA) was used to obtain the infrared spectra at 4000–400 cm^{-1} in order to study the organic bonds on the surface of zeolite samples. Before analysis, all the samples were placed in an oven for 24 h at 80°C in order to remove physically absorbed water from the zeolite surfaces. The surface morphological difference between NZ and QaNaZ was studied by scanning electron micrography (Nova-Nano SEM 430, USA) and the presence of each element and their percentages were analyzed by energy dispersive spectrometer (EDS).

2.3. Water samples and analytical methods

The synthetic water samples were prepared by dissolving prescribed initial concentrations of KH_2PO_4 (analytical grade, as P), NH_4Cl (analytical grade, as NH_4^+-N) and KNO_3 (analytical grade, as NO_3^--N) into deionized water. The municipal secondary effluent samples were collected from a Sewage Treatment Plant (Haidian district, Beijing, China) on March 20, 2016. The general water quality of the actual effluent samples was shown as follows: P = 5.16 ± 0.21 mg/L, NH_4^+-N = 6.01 ± 0.07 mg/L, NO_3^--N = 14.96 ± 0.46 mg/L, Cl^- = 73.25 ± 0.60 mg/L, SO_4^{2-} = 111.21 ± 0.83 mg/L, pH = 7.25 ± 0.20. All the samples were stored in dark at 4°C before use.

The concentrations of P and NH_4^+-N were analyzed spectro photometrically by molybdenum blue method and Nessler's reagent colorimetric method respectively, while the concentration of NO_3^--N was determined by sulfamic acid spectrophotometric method with a UV-vis spectrophotometer (Shimadzu UV-1800, Japan). Besides, the concentrations of chloride and sulfate in water samples were determined using the ion chromatography method (Dionex CS-1100, USA). The pH values were measured using a pH meter (Thermo Orion 420A, USA). All samples were analyzed in three replicates.

2.5. Adsorption experiments

Adsorption experiments were carried out with the synthetic water sample to investigate the effect of different parameters on the removal of phosphate, ammonium and nitrate by NZ and QaNaZ. For each batch adsorption experiment, specified dosage of NZ or QaNaZ was firstly added into the flask containing 100 mL synthetic water sample at prescribed initial concentration at desired pH (adjusted using 0.1 mol/L HCl or NaOH solution). Then the flask was shaken in the thermostatic shaker at 200 rpm and 298 K. 5 mL supernatant was collected as sample and then filtered through the 0.45 μm membrane before analysis.

The initial concentration, contact time, adsorbent dosage, initial pH were the parameters investigated in this study. The detailed conditions for each experiment are listed in Table 1.

2.6. Adsorption isotherms

Adsorption isotherms experiments were conducted with synthetic water samples at three temperatures 298 K, 303 K, and 308 K. The main experiments were performed as the adsorption experiments and the detailed experimental conditions are described in Table 1.

Freundlich equation [Eq. (1)] and Langmuir [Eq. (2)] [19] were used to describe the adsorption isotherm data. These equations can be expressed as follows:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{1}$$

$$\frac{C_e}{q_e} = \frac{1}{K_{L\,q_m}} + \frac{C_e}{q_m} \tag{2}$$

where q_e is the amount of ammonium or nitrate or phosphate adsorbed on per unit mass of adsorbent (mg/g); C_e is the equilibrium concentration in solution (mg/L); K_F and n are Freundlich adsorption equilibrium constants. The values of $1/n$ implied the type of isotherm and can be classified as irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$) and unfavorable ($1/n > 1$). q_m is the theoretical maximum adsorption capacity (mg/g); K_L is the Langmuir coefficients (L/mg);

The values of dimensionless parameter R_L, which is a measure of adsorption favorability, were calculated as follows:

$$R_L = \frac{1}{1 + K_L C_0} \tag{3}$$

where C_0 (mg/L) is the initial ions concentration. The R_L value indicates the type of the isotherm: unfavorable ($R_L \geq 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [20] .

2.7. Adsorption kinetics and thermodynamic studies

To evaluate the efficiency of ammonium, nitrate and phosphate adsorption processes onto QaNaZ, the pseudo-first-order model [Eq. (4)], the pseudo-second-order model [Eq. (5)], the intra-particle diffusion model [Eq. (6)] [21] and the Bangham's model [Eq. (7)] [22] were used to describe the kinetic data, as follows:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_{2\,q_e^2}} + \frac{t}{q_e} \tag{5}$$

$$q_t = k_t t^{\frac{1}{2}} + C \tag{6}$$

Table 1
Detailed experimental conditions for adsorption experiments

No	Parameter concerned	Experimental conditions			
		Initial concentration (mg/L)	Time (min)	Dosage (g/L)	pH
1	Initial concentration	P, NH4$^+_{-N}$, NO_3^-–N: 5–80	30	50	No adjustment
2	Contact time	P, NH_4^+-N: 5; NO_3^-–N: 15	0–120	50	No adjustment
3	Dosage	P, NH_4^+-N: 5; NO_3^-–N: 15	30	5–70	No adjustment
4	pH	P, NH_4^+-N: 5; NO_3^-–N: 15	30	50	2–13

$$\log\left(\frac{C_0}{C_0}-q_t m\right)=\log\left(\frac{k_0 m}{2.303V}\right)+a\log(t) \tag{7}$$

where q_e and q_t are the amounts of adsorbate adsorbed on per unit weight of adsorbent at equilibrium time and time t (mg/g); k_1 is the pseudo-first-order rate constant; k_2 is the pseudo-second-order rate constant of adsorption; k_t is the intra-particle diffusion rate constant (mg/(g·min$^{1/2}$)) and C is the intercept; V is the volume of the solution (mL); a (<1) and k_0 are constants. The value of q_t (mg/g) was calculated as follows:

$$q_t=(C_0-C_t)\frac{V}{m} \tag{8}$$

where C_0 and C_t are the initial and liquid-phase concentrations of adsorbate in solution at any time t (mg/L), respectively; q_t is the adsorbate uptake on adsorbent at any time t (mg/g); V is the volume of solution (L); m is the mass of adsorbent (g). Thermodynamic parameters such as Gibbs energy (ΔG), enthalpy (ΔG) and entropy (ΔS) for the adsorption on adsorbents were calculated as follows [15]:

$$\Delta G=-RT\ln K_0 \tag{9}$$

$$\Delta S=\frac{(\Delta H-\Delta G)}{T} \tag{10}$$

$$\ln K_0=\frac{-\Delta H}{(RT)}+\frac{\Delta S}{R} \tag{11}$$

where R is universal gas constant (8.314 J/(mol·K)); T is the temperature (K); K_0 is the equilibrium constant which can be calculated from the intercept of plot of $ln\ (Q_e/C_e)$ vs. Q_e [23].

2.8. Coexistence anion experiments

Coexistence anion experiments were performed to study the effect of chloride or sulfate on residual concentration of nitrate. The initial concentration of NO_3^--N was set as 15 mg/L while the concentrations of chloride or sulfate varied from 7.5 to 90 mg/L prepared with NaCl (analytical grade) or anhydrous Na_2SO_4 (analytical grade) respectively. In this experiment, the dosage of QaNaZ was 30 g/L at temperature of 298 K and the pH of synthetic water sample was not adjusted.

The selectivity coefficient can be used to quantitatively evaluate the ability of an ion exchanger to selectively interact with an ion present in the solution. The selectivity coefficient was defined as the ratio of these two ions in solution versus the ratio of the two ions on the QaNaZ [Eq. (12)] [24].

$$k_{NO_3^-/Cl^-}=\frac{\dfrac{[NO_3^-]_{QaNaZ}}{[Cl^-]_{QaNaZ}}}{\dfrac{[NO_3^-]_{sol}}{[Cl^-]_{sol}}} \tag{12}$$

where the subscript "QaNaZ" refers to the adsorbent phase and "sol" refers to the external solution. The selectivity coefficient is a measure of preference for a particular ion. The greater the selectivity coefficient is, the greater the preference for the ion.

2.9. Regeneration and reuse

The regeneration and reuse experiments were conducted in actual municipal secondary effluent. First of all, the freshly prepared QaNaZ was added into sewage sample at the dosage of 50 g/L to investigate the removal efficiency of phosphate, ammonium and nitrate. The saturated QaNaZ was collected. Three flasks containing 30 g saturated QaNaZ mixed with 500 mL 6%, 10% and 15% (wt%) NaCl solutions were shaken in the thermostatic shaker for 60 min at temperature of 298 K, after which the regenerated QaNaZ was washed with deionized water until no chloride residual was detected. The ion removal capacity of the regenerated QaNaZ was also evaluated with sewage sample at a dosage of 50 g/L without pH adjustment at 298 K.

3. Results and discussion

3.1. Characterization

The XRD patterns of zeolites are shown in Fig. 1. According to Fig. 1a, the most characteristic reflection peaks are assigned as the heulandite and clinoptilolite structure based on JCPDS file No 39-1383, indicating that the NZ used in this study included heulandite ($Ca_{3.6}K_{0.8}Al_{8.8}Si_{27.4}O_{72}$·26.1 H_2O) and clinoptilolite [$(NaKCa)_5Al_6Si_{30}O_{72}$·$18H_2O$] as the major components. The XRD pattern of QaNaZ (Fig. 1b) was almost the same as that of NZ without new crystalline phases or evident peaks, revealing that the structure of zeolites was not changed or damaged during the modification process.

Figs. 2a, b show the FT-IR spectra of NZ and QaNaZ samples. The characteristic bands of zeolite were present in the spectra of both NZ and QaNaZ samples [25]. Peaks at 3617 cm^{-1} and 1569 cm^{-1} were assigned to the O-H and

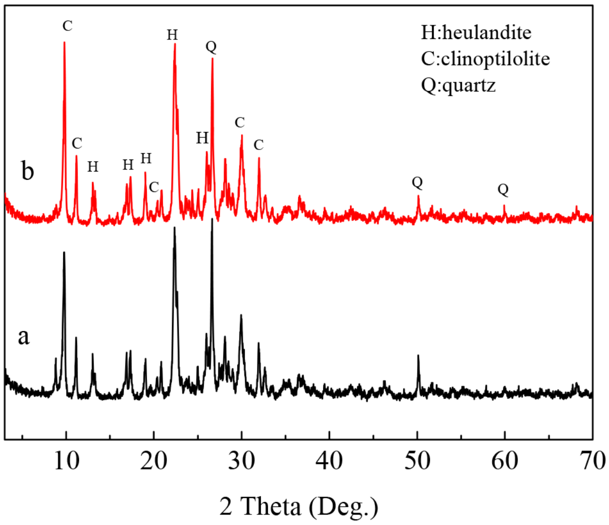

Fig. 1. XRD patterns of (a) NZ and (b) QaNaZ.

H-O-H bending vibration respectively, while peaks at 794 cm^{-1} and 516 cm^{-1} were corresponding to weak bands of T-O external symmetric stretching and O-T-O angular deformation (T indicates the tetrahedrical position of Si and Al). Meanwhile, some additional peaks were present in the spectrum of QaNaZ (Fig. 2b) [13]. Two intense absorbance bands around 2922 and 2845 cm^{-1} can be assigned to asymmetric and symmetric C-H stretching vibration of the methylene groups. Peak at 1466 cm^{-1} was the characteristic band of quaternary ammonium salt which was used during modification. These results confirmed the successful loading of quaternary ammonium groups onto the surface of QaNaZ by covalent bonding.

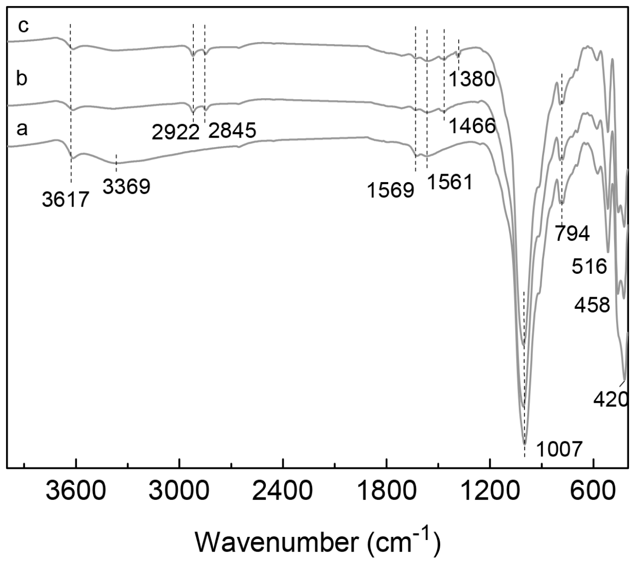

Fig. 2. FT-IR spectra of (a) NZ; (b) QaNaZ and (c) saturated QaNaZ.

The surface morphology and chemical compositions of NZ and QaNaZ samples were examined by SEM-EDS (Fig. 3). As shown in Figs. 3a, b, the coupling modification with NaCl and quaternary ammonium salt did not change the surface topography of NZ. The breakdown of some needle-like particle into less uniform and disorder particles could be caused by the mechanical force used during the grinding of zeolite samples. The chemical compositions of both NZ and QaNaZ samples are shown in Figs. 3c, d. It clearly indicated that the major chemical compositions of NZ were Al_2O_3 and SiO_2, as well as the alkaline metal ions Mg^{2+} and Ca^{2+}. The Na^+ content of QaNaZ increased significantly from 0.33% to 1.37% (atomic percentage), while the atomic percentage of Ca^{2+} and Mg^{2+} decreased respectively from 1.15% to 0.49% and 0.74% to 0.68%, which could be attributed to the exchange between Na^+ in the solution and Ca^{2+} or Mg^{2+} ions in the zeolite structure.

Based on the results of characterization, the preparation and structure of QaNaZ could be illustrated as in Fig. 4. Quaternary ammonium group-containing silane coupling agents react with hydroxyl groups on the surface of zeolite, forming Si-O bonding. Thus, the positive charge of quaternary ammonium salt groups would be attached to the zeolite by covalent bonding , which is more stable than the Coulombic and hydrophobic bonding of surfactant-mod-

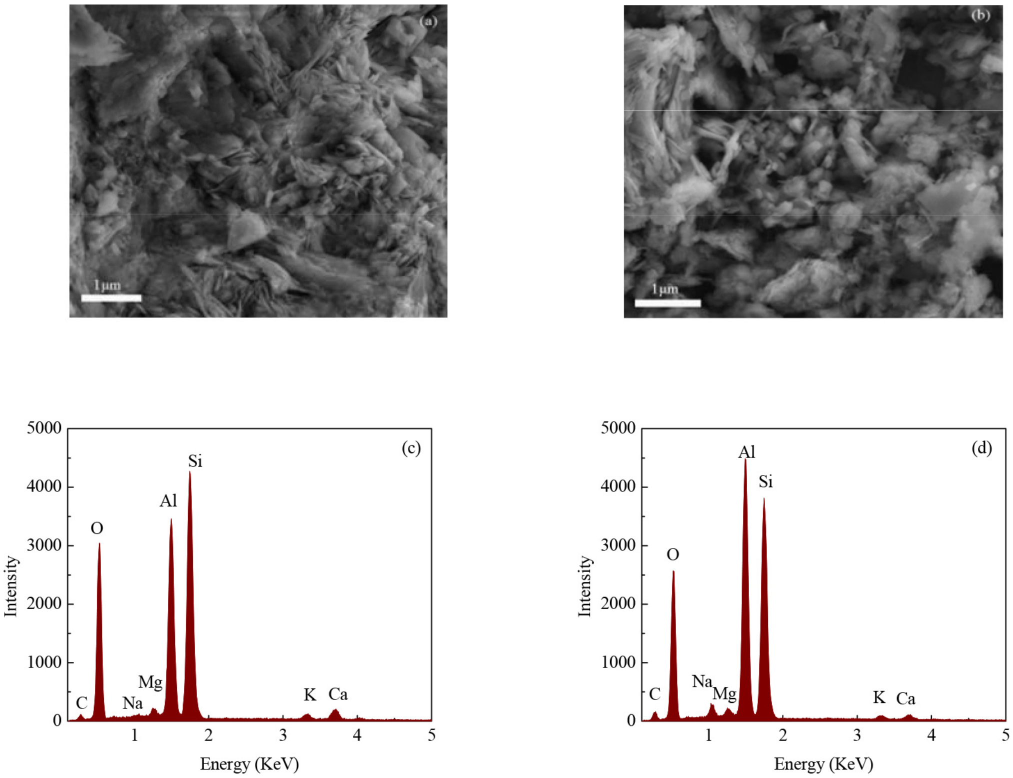

Fig. 3. SEM images of a) NZ; b) QaNaZ and the EDS spectra of c) NZ; d) QaNaZ.

ified zeolite [26]. Moreover, after impregnated in NaCl solution, Ca^{2+} or Mg^{2+} ions in the zeolite structure would be exchanged by Na^+, which have been reported to be beneficial for the cations removal by zeolite [9]. These cations located in the zeolite pore or channel are bound with aluminosilicate structure by weak electrostatic bonds, which allows exchange with certain cations (e.g. NH_4^+) in solution [27].

3.2. Adsorption studies

The results of phosphate, ammonium and nitrate adsorption by NZ and QaNaZ in synthetic water are shown in Fig. 5. Fig. 5a illustrates the effect of initial concentration on phosphate, ammonium and nitrate removal when the dosage of NZ and QaNaZ was 50 g/L at 298 K. Compared with the NZ, QaNaZ exhibited more than 20% higher removal efficiency of NH_4^+-N in spite of the change of initial concentration. This observation could be attributed to the higher Na^+ ions for QaNaZ, and the absorbed Na^+ ions were readily exchanged by ammonium on zeolite surfaces [9]. More importantly, it was obvious that NZ could only remove ammonium, while QaNaZ could remove ammonium, phosphate, and nitrate simultaneously, suggesting that loading of quaternary ammonium groups onto the zeolite surface by covalent bonding contributed to the adsorption of anions (i.e. phosphate, and nitrate) onto QaNaZ.

Furthermore, in order to better evaluate the performance of QaNaZ in practical water treatment, the initial concentrations of phosphate, ammonium and nitrate were set at 5 mg/L, 5 mg/L and 15 mg/L respectively, according to first level B criteria specified in national effluent standard in China (GB 18918-2002) [4]. Fig. 5b depicts the effect of contact time on adsorption of phosphate, ammonium and nitrate onto NZ and QaNaZ. It shows that phosphate, ammonium and nitrate were adsorbed rapidly by QaNaZ during the first 20 min and the adsorption reached equilibration within 30 min. Additionally, residual concentrations of P, NH_4^+-N and NO_3^--N decreased with the increasing dosage of QaNaZ (Fig. 5c). This is because of the larger contact area and the more surface active sites with the increase of adsorbent dosage [15,28,29]. The residual concentrations of P, NH_4^+-N and NO_3^--N decreased to 0.012 mg/L, 2.65 mg/L and 0.38 mg/L respectively at the QaNaZ dosage of 50 g/L. However, the removal efficiency of the target pollutants did not increase further when the dosage increased to more than 50 g/L, which is due to particle aggregation or particle deposition under a high solid-liquid ratio [30].

Effect of pH on the removal efficiency of phosphate, ammonium and nitrate by NZ and QaNaZ was also studied (Fig. 5d). It was observed that the adsorption of ammonium was a pH-dependent process: ammonium would be adsorbed by QaNaZ more efficiently at pH from 5 to 8 (the residual concentration of NH_4^+-N would drop to less than 3.0 mg/L); decreasing pH to lower than 5 would result in decrease of ammonium removal, principally being attributed to the increase in competing hydrogen ions; the increase in pH would also reduce ammonium removal, especially at pH > 8, probably owing to the formation of $NH_3{\cdot}H_2O$ instead of ammonium as the main existing form in alkaline solutions. This observation was consistent with previous studies [9]. However, the removal of phosphate and nitrate by QaNaZ was not significantly affected by pH. Hence, the optimal solution pH for simultaneous removal of phosphate, ammonium and nitrate by QaNaZ was from 5 to 8.

In general, QaNaZ exhibited more advantages than NZ in simultaneous removal of phosphate, ammonium and nitrate according to the results of adsorption studies. The excellent performance of QaNaZ on removing phosphorus and nitrogen would contribute to its potential applications in waste water treatment.

3.3. Adsorption isotherms

The adsorption isotherm describes the relationship between the amounts of adsorbate adsorbed on the adsorbent (q_e) to the adsorbate concentration at equilibrium

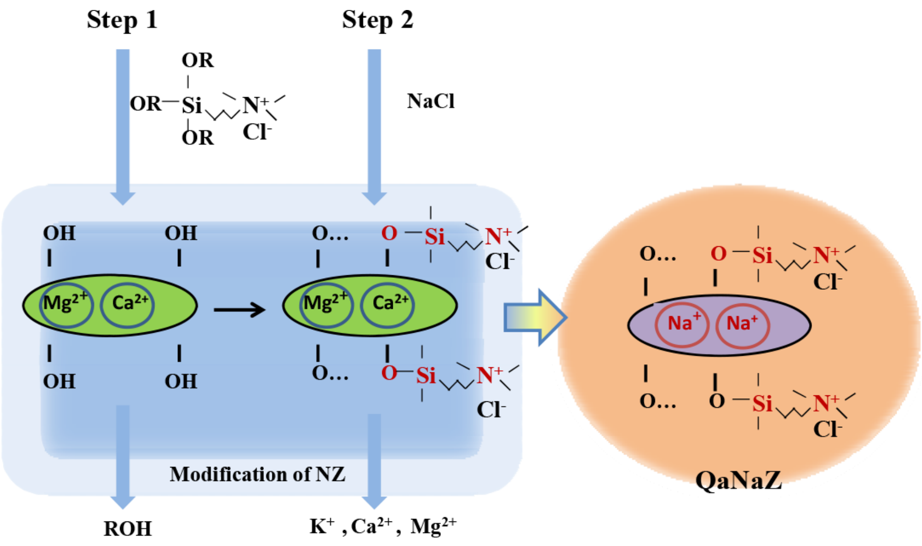

Fig. 4. Schematic representation of the preparation and structure of QaNaZ.

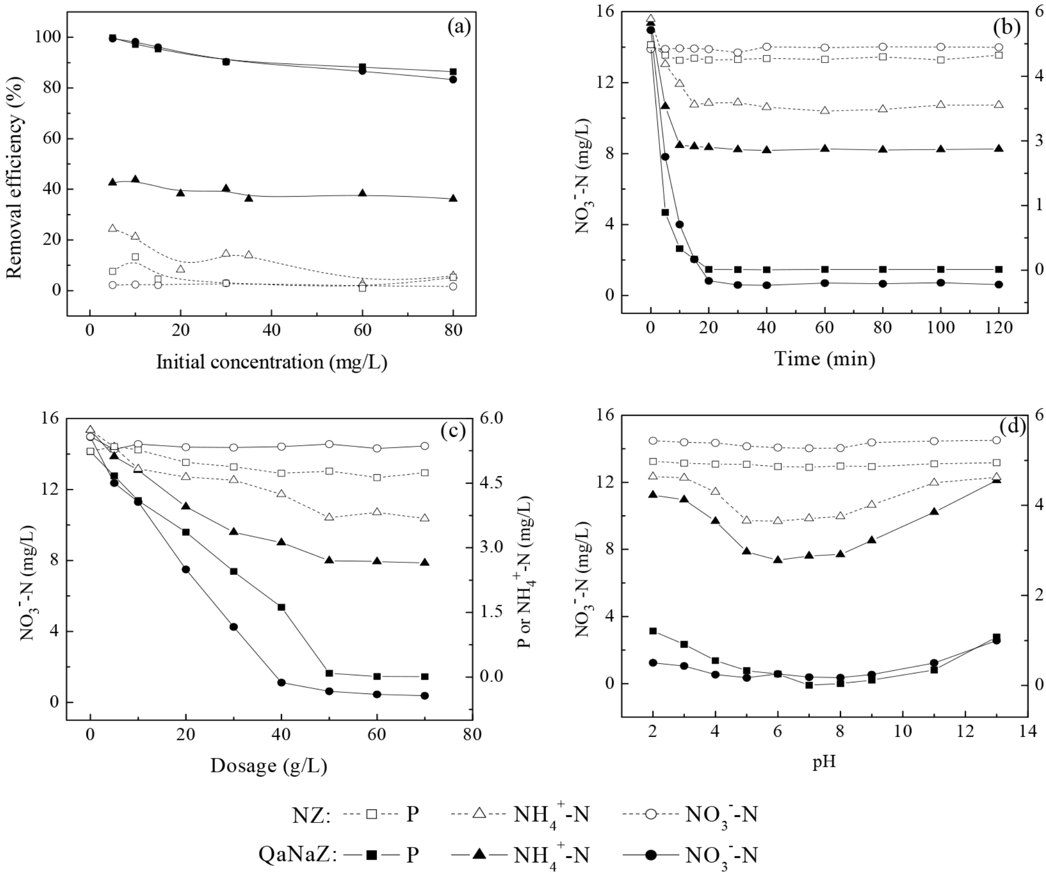

Fig. 5. Effects of different factors (a) initial concentration, (b) time, (c) dosage, and (d) pH on ammonium, phosphate, and nitrate removal by NZ and QaNaZ in synthetic water sample. Time of a, c, d: 30 min; dosage of a, b, d: 50 g/L; pH of a, b, c: without adjustment; initial NH$_4^+$-N, P, NO$_3^-$-N concentration of b, c, and d: 5 mg/L, 5 mg/L, 15 mg/L; temperature: 298 K.

condition (C_e) at a constant temperature [31]. It provides important physic-chemical information for the description of how adsorbate molecules interact with adsorbent surface, which is essential for understanding the characteristics of adsorption systems. Adsorption isotherms of Langmuir and Freundlich removal of phosphate, ammonium and nitrate by QaNaZ in synthetic water sample at different temperatures (298 K, 303 K and 308K) are presented in Fig. 6 and isotherm constants are also listed in Table 2.

As shown in Table 2, both Freundlich and Langmuir isotherms fitted well with the experimental data of phosphate, ammonium and nitrate adsorption onto QaNaZ with correlation coefficient (R^2) significantly higher than 0.9, indicating involvement of both physisorption and chemisorption in this process [32]. Moreover, Langmuir model described the equilibrium data with higher R^2 (>0.999), suggesting that the adsorption principally occurred on a homogeneous surface by monolayer adsorption. Additionally, the calculated values of q_e and q_m in Langmuir model, which represented the equilibrium adsorption and maximum capacity of ions on the adsorbent, showed slight fluctuation with the increase of temperature (Table 2). It revealed that the temperature had little influence on the removal of phosphate, ammonium and nitrate by QaNaZ. Moreover, all the R_L values were below 1, indicating a favorable nature of phosphate, ammonium and nitrate adsorption onto QaNaZ under various temperature conditions in this study [33] Therefore, our results strongly demonstrated that QaNaZ is a type of suitable adsorbent for the removal of phosphate, ammonium and nitrate in aqueous system.

3.4. Adsorption kinetics and thermodynamics

Four kinetic models were used to describe the rate of adsorption and elucidate the adsorption mechanism of phosphate, ammonium, and nitrate on QaNaZ. The constants of Pseudo-first-order, pseudo-second-order and Bangham's equation kinetic models were calculated and are listed in Table 3, while the Intra-particle diffusion model is shown in Fig. 7.

As shown in Table 3, because all R^2 obtained from pseudo second-order model (> 0.989) were much higher than those of pseudo first-order model (approximately 0.869), it was concluded that pseudo-second-order model could better describe the kinetics of adsorption of phosphate, ammonium, and nitrate on QaNaZ, which assumes that chemical adsorption rather than physical adsorption is the main adsorption mechanism [34].

Adsorbate migration from solution to the surface of adsorbent occurs gradually and this process is often controlled by one or several steps, such as liquid film diffusion, pore diffusion, surface diffusion and adsorption

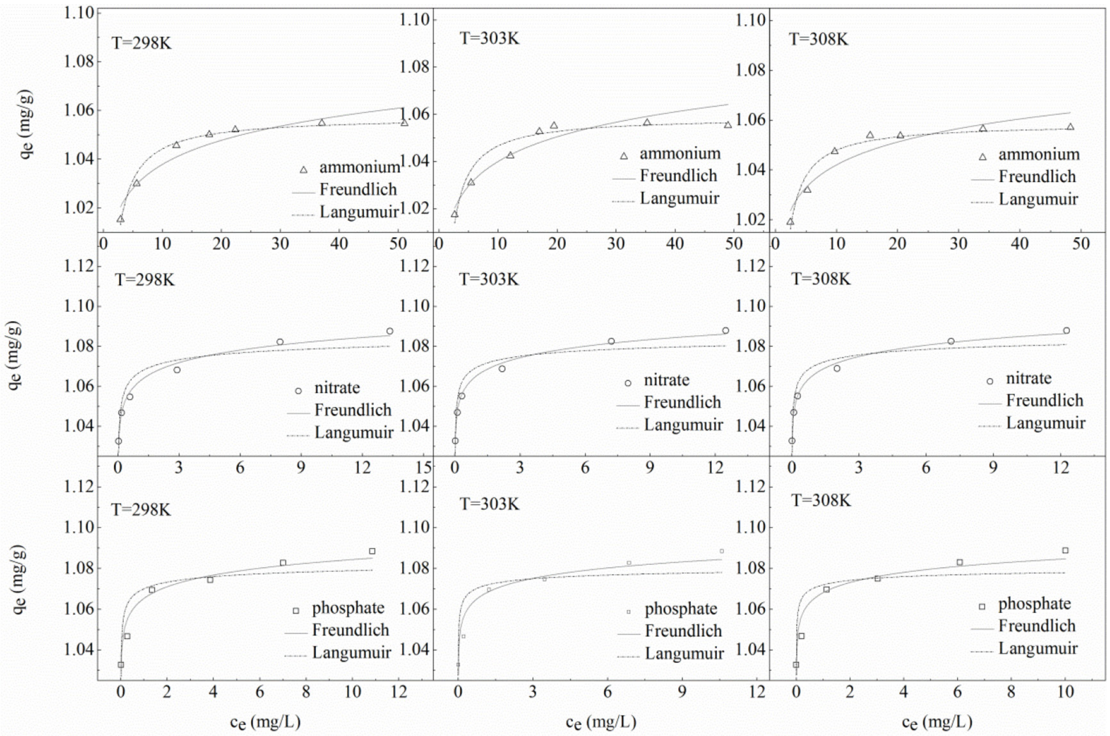

Fig. 6. Isotherms of Langmuir and Freundlich on ammonium, phosphate, nitrate removal by QaNaZ in synthetic water sample. Initial concentration of NH_4^+-N, NO_3^--N or P: 5 – 80 mg/L; dosage: 50 g/L; time : 30 min; pH :without adjustment.

Table 2
Isotherms constants for ammonium, phosphate, nitrate by QaNaZ at different temperatures

Constants	Ammonium			Nitrate			Phosphate		
	298 K	303 K	308 K	298 K	303 K	308 K	298 K	303 K	308 K
Freundlich									
K_f	1.0019	1.0037	1.9985	1.0621	1.0654	1.0661	1.0653	1.0671	1.0681
$1/n$	0.0155	0.0156	0.0146	0.0084	0.0076	0.0075	0.0076	0.0067	0.0066
R^2	0.9432	0.9459	0.9173	0.9842	0.9912	0.9938	0.9408	0.9244	0.9193
Langmuir									
q_m (mg/g)	1.0578	1.0587	1.0597	1.0877	1.0878	1.0878	1.0883	1.0883	1.0887
q_e (mg/g)	1.0547	1.0552	1.0571	1.0876	1.0879	1.0878	1.0883	1.0883	1.0887
K_L (L/mg)	0.1328	0.1204	0.1108	0.0202	0.0145	0.0134	0.0202	0.0181	0.0167
R^2	1.0000	0.9999	1.0000	0.9999	0.9999	1.0000	0.9999	0.9999	0.9999
R_L	0.6010	0.6242	0.6180	0.7675	0.8214	0.8326	0.8958	0.9056	0.9122

on the pore surface, or a combination of several steps through the adsorption process [22]. Bangham's equation is used to check whether pore diffusion is the only rate controlling step in the adsorption system according to kinetic data. However, our experimental data were not well fitted to Bangham 's model due to its relatively low correlation coefficients (<0.615) shown in Table 3. It revealed that the diffusion of adsorbate into pores of the sorbent is not the only rate controlling step. In addition, the influence of intra-particle diffusion on adsorption process can be studied through the intra-particles diffusion model [9]. Fig. 7 shows that the plots of q_t versus $t^{1/2}$ for ammonium, phosphate and nitrate adsorption onto QaNaZ exhibited two separate phases, especially for that of nitrate adsorption. These two phases could be attributed to the external surface adsorption and final equilibrium stage, respectively. In addition, the plot curves did not intercept the origin (0,0), indicating that the intraparticle diffusion was not the only rate controlling step, and some other processes may control the rate of adsorption [22].

To determine whether the adsorption process could happen spontaneously, thermodynamic parameters Gibbs energy (ΔG), enthalpy (ΔG) and entropy (ΔS) were cal-

Table 3
Kinetic parameters for pseudo-first-order, pseudo-second-order and Bangham's models

Adsorbate	Pseudo-first-order				Pseudo-second-order				Bangham		
	q^a (mg/g)	K_1 (min^{-1})	q_e (mg/g)	R^2	q^a (mg/g)	K_2 (g/ mg·min)	q_e (mg/g)	R^2	K_0	α	R^2
Ammonium	0.059	0.1209	0.0136	0.8692	0.059	15.4052	0.0607	0.9996	0.9816	0.0115	0.6148
Nitrate	0.2876	0.2552	0.3945	0.8698	0.2876	0.587	0.3327	0.9898	1.4591	0.0723	0.5566
Phosphate	0.1044	0.2434	0.0943	0.8682	0.1044	5.7162	0.1095	0.999	1.8128	0.0269	0.5443

q^a is the actual adsorption quantity obtained from the experiment

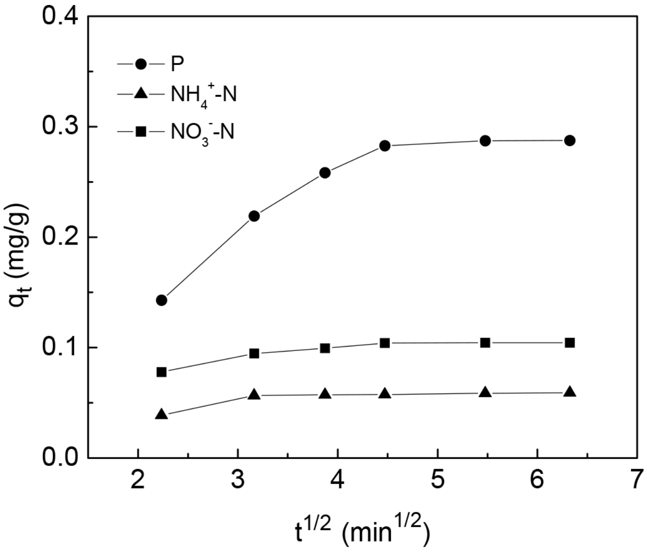

Fig. 7. Intra-particle diffusion model for ammonium, phosphate, nitrate adsorption onto QaNaZ in synthetic water.

culated using Eqs. (9), (10) and (11) and are shown in Table 4. The negative ΔG revealed that the adsorption of phosphate, ammonium and nitrate onto QaNaZ was spontaneous, and more negative ΔG at higher temperatures indicated that the adsorption was favorable at high temperatures [35]. This is in agreement with positive ΔH values (9.955, 3.305, and 8.785 kJ/mol), indicating the endothermic nature of the adsorption process. The positive ΔS (0.074, 0.045 and 0.069 kJ/ mol K) indicated that the randomness was increased at the solid-solution interface during the adsorption.

Based on the results of adsorption kinetics and thermodynamics, we concluded that the adsorption of phosphate, ammonium and nitrate onto QaNaZ probably occurred with surface exchange reactions (i.e. ion exchange) until functional sites of adsorbent were completely filled. The adsorbed molecules would subsequently diffuse into the QaNaZ and other interactions could take place. This conclusion could be also evidenced by FT-IR spectra of saturated QaNaZ (Fig. 2c), which showed a new peak at 1380 cm^{-1} compared with the FT-IR spectra of unused QaNaZ (Fig. 2b). This peak could be assigned to N-O stretching vibration of nitrate absorbed on QaNaZ. The proposed mechanism of phosphate, ammonium and nitrate adsorption onto QaNaZ is depicted in Fig. 8.

3.5. Effect of coexisting anions

Sewage contains a variety of ions, and some of which may compete with phosphate, ammonium and nitrate for the active adsorption sites. Thus, it is important to investigate the potential interference of coexisting ions on adsorption onto adsorbent. In fact, numerous previous studies have investigated the effect of coexisting cations on ammonium adsorption onto zeolites. The presence of some typical coexisting cations in wastewater, such as Na^+, K^+, Ca^{2+}, and Mg^{2+}, would affect ammonium uptake on zeolite [36]. In addition, due to the high solubility of nitrate in water, it can only be transferred from liquid phase to solid phase through ion exchange on the surface of QaNaZ, while phosphate can also be removed from water through deposition or complexation with metal compounds. Accordingly, it seems that the adsorption of nitrate onto QaNaZ could be more easily affected by coexisting anions. Hence, we investigated the effect of coexisting anions on the removal of nitrate by QaNaZ in the present study. Chloride and sulfate ions were selected as the coexisting anions to be investigated because of their common presence in sewage.

Figs. 9a and b show the adsorption equilibrium of nitrate in the mixed solution. Both chloride and sulfate should have negative influence on the removal of nitrate by QaNaZ, because the concentration of residual nitrate increased from 4.00 mg/L to 6.12 mg/L and 11.77 mg/L with the increase of initial concentration of chloride and SO_4^2 in mixed solution respectively. Moreover, the selectivity coefficient ($k_{NO_3^-/Cl^-}$ and $k_{NO_3^-/SO_4^{2-}}$) was used in this study to quantitatively characterize the ability of QaNaZ to select one of two ions present in the solution. The selectivity coefficient is defined as the ratio of the two ions in solution versus the ratio of the two ions on the adsorbent. As shown in Figs. 9c and d, the selectivity coefficient of the QaNaZ for nitrate versus chloride and sulfate was determined to be 8.0270 and 0.5308, respectively. It suggested that the selectivity order of the three anions by QaNaZ was sulfate > nitrate > chloride. Certainly, the adsorption of these anions onto QaNaZ would principally depend on their initial concentrations.

3.6. Regeneration and reuse

In order to evaluate the performance of regenerated QaNaZ, the regeneration and reuse experiments of QaNaZ were conducted with actual municipal secondary effluent sample. The initial concentrations of P, NH_4^+-N, NO_3^--N, Cl^-, and SO_4^{2-} in sewage sample were 5.16, 6.01, 14.96, 73.25, 111.21 mg/L, respectively. As shown in Fig. 10, the removal

Table 4
Thermodynamic parameters of adsorption onto QaNaZ in synthetic water samples

T (K)	Ammonium			Nitrate			Phosphate		
	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol·K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol·K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol·K)
298	–10.083	3.305	0.045	–11.807	8.785	0.069	–11.951	9.955	0.074
303	–10.248			–12.26			–12.434		
308	–10.533			–12.497			–12.685		

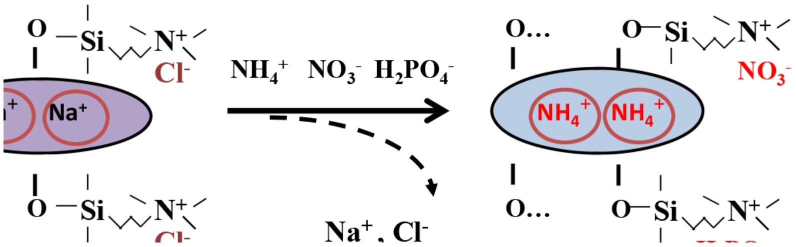

Fig. 8. Mechanism of ammonium, nitrate and phosphate adsorption onto QaNaZ.

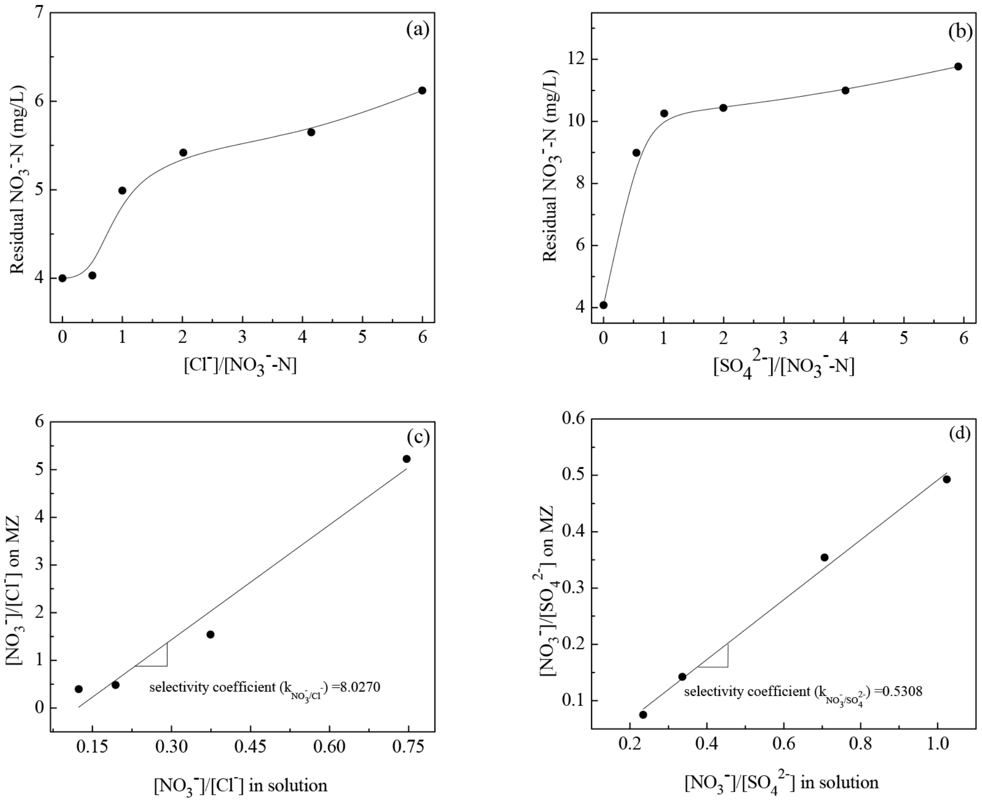

Fig. 9. Effect of common ion (a) chloride and (b) sulfate on the adsorption of residual nitrate onto QaNaZ in synthetic water sample. Adsorption equilibrium of QaNaZ in different mixed solutions of (c) nitrate and chloride or (d) nitrate and sulfate. QaNaZ dosage: 30 g/L; initial NO_3^--N concentration: 15 mg/L; chloride or sulfate in samples: 7.5 – 90 mg/L; time: 30 min; pH: without adjustment; temperature: 298 K.

efficiency of P, NH_4^+-N and NO_3^--N by freshly prepared QaNaZ reached 94.18%, 48.84%, and 91.11% at dosage of 50 g/L, which was slightly less than that in synthetic water sample with similar initial concentrations (99.8%, 42.6% and 96.13%, respectively). The low efficiency of NH_4^+ adsorption may be resulted from the high diffusion resistance of NH_4^+ in the pores and channels of zeolites. The result revealed that the coexistence of ions and compounds in actual sew-

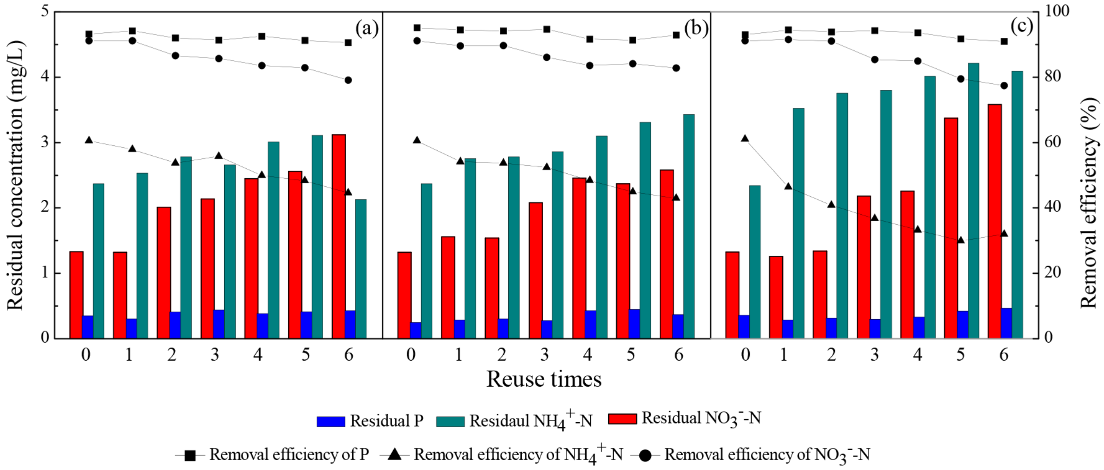

Fig. 10. Effect of QaNaZ regeneration by (a) 6% NaCl, (b) 10% NaCl, and (c) 15% NaCl solutions on the removal of contaminants in sewage sample. Dosage: 50 g/L; initial concentration of NH_4^+-N, NO_3^--N, P, Cl^-, SO_4^{2-} in sewage sample: 6.01, 14.96, 5.16, 73.25, 111.21 mg/L; initial pH of sample: 7–7.5; time: 30 min; temperature: 298 K.

age would have some but not significant negative influence on the phosphorous and nitrogen removal by QaNaZ.

Moreover, the regeneration and reuse of adsorbent would reduce cost in practical applications and be more environment friendly. According to the commonly used methods for adsorbent regeneration, we used different initial concentrations of NaCl solution (6%, 10% and 15%, mass percentage) to regenerate QaNaZ. As shown in Fig. 10, there was no significant difference observed in removal efficiency of P, NH_4^+-N and NO_3^--N among QaNaZ regenerated by different initial concentrations of NaCl solution. Thus, initial concentration of 6 w% NaCl solution was used to regenerate the saturated QaNaZ.

Furthermore, according to Fig. 10a, after QaNaZ was regenerated by 6 w% NaCl solution and reused for 6 times, the removal efficiency for P and NH_4^+-N still maintained at about 90–95% and 50–60% respectively, while the removal efficiency for NO_3^--N declined slightly from 91.11% to 79.14%. These results indicated that the saturated QaNaZ could be regenerated by NaCl solution. We postulated that the high capacity of regenerated QaNaZ was attributed to the stable covalent bonding between the quaternary ammonium groups and the surface of zeolite. Meanwhile, it should be noted that the concentrations of P, NH_4^+-N and NO_3^--N in the municipal secondary effluent used in this study only met the first level B criteria specified in national effluent standard (GB 18918-2002) [4] in China. Their concentrations decreased to less than 0.5 mg/L, 5 mg/L and 5 mg/L respectively after treated by freshly prepared or regenerated QaNaZ, which met the firs level A criteria. In general, due to its high removal efficiency of phosphorous and nitrogen, as well as its simple and cost-effective regeneration, QaNaZ could be regarded as an efficient adsorbent for the simultaneous removal of phosphate, ammonium and nitrate in waste water.

4. Conclusions

We prepared Na-pretreated zeolite covalently bonded with quaternary ammonium, which efficiently removed ammonium, phosphate, and nitrate in aqueous solution simultaneously. Characterization of QaNaZ by XRD, FT-IR and SEM-EDS showed that quaternary ammonium groups were successfully attached onto the surface of QaNaZ by stable covalent bonding. QaNaZ exhibited outstanding adsorption performance for phosphate, ammonium, and nitrate in a wide range of pHs (5–8) with a short equilibration time of 30 min. The adsorptions of phosphate, ammonium, and nitrate onto QaNaZ were well fitted with both Langmuir and Freundlich isotherm indicating involvement of both physisorption and chemisorption in the process, while chemical adsorption was found to be the main adsorption mechanism. This adsorption process was spontaneous according to the results of thermodynamic studies. We concluded that surface exchange reactions (i.e. ion exchange) probably occurred at the beginning of the adsorption until functional sites of QaNaZ were completely filled, followed by intra-particle diffusion and other interactions into QaNaZ. Coexisting ions in municipal secondary effluent such as chloride and sulfate did not show significant interference on the removal efficiency of phosphate, ammonium, and nitrate by QaNaZ. Water quality of substandard municipal sewage was improved greatly to meet the discharge or reuse standard after treated by QaNaZ. Moreover, the saturated QaNaZ could be regenerated and its adsorption capacity recovered by treatment with NaCl solution. This work provided an efficient adsorbent for the simultaneous removal of phosphate, ammonium and nitrate with high removal efficiency and good regeneration capacity, which will have broad application prospects in wastewater treatment.

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References

[1] R. Li, L. Morrison, G. Collins, A. Li, X. Zhan, Simultaneous nitrate and phosphate removal from wastewater lacking organic matter through microbial oxidation of pyrrhotite coupled to nitrate reduction, Water Res., 96 (2016) 32–41.

[2] M. Lurling, E. Mackay, K. Reitzel, B.M. Spears, Editorial - A critical perspective on geo-engineering for eutrophication management in lakes, Water Res., 97 (2016) 1–10.

[3] A.M.E. Khalil, O. Eljamal, S. Jribi, N. Matsunaga, Promoting nitrate reduction kinetics by nanoscale zero valent iron in water via copper salt addition, Chem. Eng. J., 287 (2016) 367–380.

[4] Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant in China, GB/T189182002, Environmental Science Press of China, Beijing, China, 2002 (in Chinese).

[5] H. Gao, M. Liu, J.S. Griffin, L. Xu, D. Xiang, Y.D. Scherson, W.T. Liu, G.F. Wells, Complete nutrient removal coupled to nitrous oxide production as a bioenergy source by denitrifying polyphosphate-accumulating organisms, Environ. Sci. Technol., 51 (2017) 4531–4540.

[6] S. Yao, L. Chen, D. Guan, Z. Zhang, X. Tian, A. Wang, G. Wang, Q. Yao, D. Peng, J. Li, On-site nutrient recovery and removal from source-separated urine by phosphorus precipitation and short-cut nitrification-denitrification, Chemosphere, 175 (2017) 210–218.

[7] G. Montegut, L. Michelin, J. Brendle, B. Lebeau, J. Patarin, Ammonium and potassium removal from swine liquid manure using clinoptilolite, chabazite and faujasite zeolites, J. Environ. Manage., 167 (2016) 147–155.

[8] J. Yuan, J. Yang, H. Ma, C. Liu, Crystal structural transformation and kinetics of NH$_4^+$/Na$^+$ ion-exchange in analcime, Microporous Mesoporous Mater., 222 (2016) 202–208.

[9] L. Lin, Z. Lei, L. Wang, X. Liu, Y. Zhang, C. Wan, D.-J. Lee, J.H. Tay, Adsorption mechanisms of high-levels of ammonium onto natural and NaCl-modified zeolites, Sep. Purif. Technol., 103 (2013) 15–20.

[10] Y. He, H. Lin, Y. Dong, Q. Liu, L. Wang, Simultaneous removal of ammonium and phosphate by alkaline-activated and lanthanum-impregnated zeolite, Chemosphere, 164 (2016) 387–395.

[11] M. Hermassi, C. Valderrama, N. Moreno, O. Font, X. Querol, N. Batis, J.L. Cortina, Powdered Ca-activated zeolite for phosphate removal from treated waste-water, J. Chem. Technol. Biotechnol., 91 (2016) 1962–1971.

[12] N. Karapinar, Application of natural zeolite for phosphorus and ammonium removal from aqueous solutions, J. Hazard. Mater., 170 (2009) 1186–1191.

[13] D. Bhardwaj, M. Sharma, P. Sharma, R. Tomar, Synthesis and surfactant modification of clinoptilolite and montmorillonite for the removal of nitrate and preparation of slow release nitrogen fertilizer, J. Hazard. Mater., 227–228 (2012) 292–300.

[14] R. Malekian, J. Abedi-Koupai, S.S. Eslamian, Influences of clinoptilolite and surfactant-modified clinoptilolite zeolite on nitrate leaching and plant growth, J. Hazard. Mater., 185 (2011) 970–976.

[15] Y. Zhan, J. Lin, Z. Zhu, Removal of nitrate from aqueous solution using cetylpyridinium bromide (CPB) modified zeolite as adsorbent, J. Hazard. Mater., 186 (2011) 1972–1978.

[16] P. Chutia, S. Kato, T. Kojima, S. Satokawa, Adsorption of As(V) on surfactant-modified natural zeolites, J. Hazard. Mater., 162 (2009) 204–211.

[17] J. Schick, P. Caullet, J.-L. Paillaud, J. Patarin, C. Mangold-Callarec, Batch-wise nitrate removal from water on a surfactant-modified zeolite, Microporous Mesoporous Mater., 132 (2010) 395–400.

[18] P. Vassileva, D. Voikova. Investigation on natural and pretreated Bulgarianclinoptilolite for ammonium ions removal from aqueous solutions. J. Hazard. Mater., 170 (2009) 948–953.

[19] X. Xu, B. Gao, Y. Zhao, S. Chen, X. Tan, Q. Yue, J. Lin, Y. Wang, Nitrate removal from aqueous solution by Arundo donax L. reed based anion exchange resin, J. Hazard. Mater., 203–204 (2012) 86–92.

[20] S. Liu, Y. Ding, P. Li, K. Diao, X. Tan, F. Lei, Y. Zhan, Q. Li, B. Huang, Z. Huang, Adsorption of the anionic dye Congo red from aqueous solution onto natural zeolites modified with N,N-dimethyl dehydroabietylamine oxide, Chem. Eng. J., 248 (2014) 135–144.

[21] J.P. Soetardji, J.C. Claudia, Y.-H. Ju, J.A. Hriljac, T.-Y. Chen, F.E. Soetaredjo, S.P. Santoso, A. Kurniawan, S. Ismadji, Ammonia removal from water using sodium hydroxide modified zeolite mordenite, RSC Adv., 5 (2015) 83689–83699.

[22] E. Alver, A.Ü. Metin, Anionic dye removal from aqueous solutions using modified zeolite: Adsorption kinetics and isotherm studies, Chem. Eng. J., 200–202 (2012) 59–67.

[23] A. Gunay, E. Arslankaya, I. Tosun, Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics, J. Hazard. Mater., 146 (2007) 362–371.

[24] Y.-J. Kim, J.-H. Kim, J.-H. Choi, Selective removal of nitrate ions by controlling the applied current in membrane capacitive deionization (MCDI), J. Membr. Sci., 429 (2013) 52–57.

[25] B. Muir, J. Matusik, T. Bajda, New insights into alkylammonium-functionalized clinoptilolite and Na-P1 zeolite: Structural and textural features, Appl. Surf. Sci., 361 (2016) 242–250.

[26] S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, Chem. Eng. J., 156 (2010) 11–24.

[27] N. Widiastuti, H. Wu, H.M Ang, D.K. Zhang, Removal of ammonium from grey water using natural zeolite, Desalination, 277 (2011) 15–23.

[28] M. Zhang, H. Zhang, D. Xu, L. Han, D. Niu, B. Tian, J. Zhang, L. Zhang, W. Wu, Removal of ammonium from aqueous solutions using zeolite synthesized from fly ash by a fusion method, Desalination, 271 (2011) 111–121.

[29] M.S. Onyango, D. Kuchar, M. Kubota, H. Matsuda, Adsorptive removal of phosphate ions from aqueous solution using synthetic zeolite, Ind. Eng. Chem. Res., 46 (2007) 894–900.

[30] M. Zieliński, M. Zielińska, M. Dębowski, Ammonium removal on zeolite modified by ultrasound, Desal. Water Treat., 57 (2015) 8748–8753.

[31] E. Wibowo, M. Rokhmat, M. Abdullah, Reduction of seawater salinity by natural zeolite (Clinoptilolite): Adsorption isotherms, thermodynamics and kinetics, Desalination, 409 (2017) 146–156.

[32] S.S. Mayakaduwa, I. Herath, Y.S. Ok, D. Mohan, M. Vithanage, Insights into aqueous carbofuran removal by modified and non-modified rice husk biochars, Environ. Sci. Pollut. Res., (2016) DOI 10.1007/s11356-11016-17430-11356.

[33] Y. Xie, S. Li, G. Liu, J. Wang, K. Wu, Equilibrium, kinetic and thermodynamic studies on perchlorate adsorption by cross-linked quaternary chitosan, Chem. Eng. J., 192 (2012) 269–275.

[34] S. Yang, J. Li, D. Shao, J. Hu, X. Wang, Adsorption of Ni (II) on oxidized multi-walled carbon nanotubes: effect of contact time, pH, foreign ions and PAA, J. Hazard. Mater., 166 (2009) 109–116.

[35] R. Han, Y. Wang, Q. Sun, L. Wang, J. Song, X. He, C. Dou, Malachite green adsorption onto natural zeolite and reuse by microwave irradiation, J. Hazard. Mater., 175 (2010) 1056–1061.

[36] X. Guo, L. Zeng, X. Li, H.S. Park, Removal of ammonium from RO permeate of anaerobically digested wastewater by natural zeolite, Sep. Sci. Technol., 42 (2007) 3169–3185.