Simultaneous removal of ammonium and nitrate by HDTMA-modified zeolite
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ABSTRACT
In this study, surfactant (hexadecyltrimethylammonium, HDTMA) modified zeolite (clinoptilolite) (SMZ) was used for simultaneous removal of ammonium and nitrate in wastewater, and the sorption properties of SMZ were determined. Results showed that natural clinoptilolite had good affinity for ammonium, but low sorption ability for nitrate, and the ammonium sorption process was well described by the pseudo-second order kinetic model. The SMZ had a significant enhancement on nitrate sorption and could simultaneously remove ammonium and nitrate at specific conditions, with removal efficiency up to 93.6% and 81.8%, respectively. The sorption process fitted well with the Langmuir isotherm. Orthogonal experiments showed that ammonium concentration was the most important factor for ammonium sorption on SMZ. However, surfactant loading was the major factor for nitrate sorption. Meanwhile, phosphate did not interfere with nitrate removal. Semi-empirical quantum mechanics molecular simulation indicated that electrostatic attraction existed between HDTMA and nitrate. Results of this study demonstrated that SMZs may have great potential for removing cations and anions simultaneously in the aquatic environment.

Key words | ammonium, HDTMA, nitrate, sorption, zeolite

INTRODUCTION
Natural zeolites (e.g. clinoptilolite, a kind of zeolite that is globally widespread), with large specific surface area, high sorption ability and cation exchange capacity (Zhang 1986), have been used widely for removing cations like heavy metals and ammonium in water (Du et al. 2005). However, zeolites with their negative charge framework are unable to remove anions from aqueous solution by sorption (Faghihian & Bowman 2005). Recently, the use of surfactant-modified zeolites (SMZs) has been reported for improving removal of inorganic anions in wastewater. Surfactant, here referring to cationic surfactant, can form bilayers or patchy bilayers with positively charged head groups on the zeolite surface to sorb anions (Li et al. 1998).

Among cationic surfactants, quaternary ammonium salt is very common, and alkylpyridinium halide follows it. They generally involve eight to 16 carbons in their long alkyl chain (Zhao 2003). However, only a few studies have reported about using alkylpyridinium SMZs for sorption of anions (Zhan et al. 2011). Currently, hexadecyltrimethylammonium (HDTMA), containing 16 carbons and thus being relatively longer than other quaternary ammonium salts, is usually used for modifying zeolite to sorb anions, such as chromate (Li & Bowman 1997), arsenate (Yusof & Malek 2009), nitrate (Guan et al. 2010), antimonite (Wingenfelder et al. 2006), and phosphate (Hrenovic et al. 2008). For nitrate, HDTMA-modified zeolites can significantly increase the maximum sorption capacity in the range of
1.49–6.63 mg/g (Li 2003; Guan et al. 2010; Schick et al. 2010) with a removal efficiency up to 80% (Schick et al. 2010). Thermogravimetric analysis demonstrated that HDTMA bilayers on the SMZs are in the order of Australian zeolite < Chinese zeolite < Croatian zeolite < US zeolite, and nitrate removal is in the same order for the four SMZs (i.e. the US SMZ has the highest sorption for nitrate) (Guan et al. 2010). Anion exchange and electrostatic attraction were the main mechanism for nitrate sorption on SMZs (Li & Bowman 1997; Guan et al. 2010; Zhan et al. 2011). The presence of possible competing anions such as bicarbonate, sulphate and chloride ions at equivalent concentrations did not significantly change the nitrate removal efficiency (Schick et al. 2010; Zhan et al. 2011). In addition, desorption of the HDTMA attached onto the zeolite surface was negligible (Schick et al. 2010).

Although SMZ can simultaneously remove cations and anions (Lenka et al. 2008), sufficient information is not available on using SMZ for simultaneous removal of ammonium and nitrate. Particularly, information is lacking on competition between phosphate (a kind of common coexisting anion) and nitrate for sorption onto SMZs. Moreover, while sorption mechanisms were determined experimentally, the sorption process on SMZs by semi-empirical quantum mechanics molecular dynamics simulation has not been evaluated.

To fill these knowledge gaps, the objectives of this study were to: (1) investigate the simultaneous removal of ammonium and nitrate by HDTMA-modified zeolites; (2) evaluate the competing effect of coexisting phosphate on removal of nitrate; and (3) elucidate the mechanism of nitrate sorbed on SMZs with semi-empirical quantum mechanics molecular dynamics simulation.

MATERIALS AND METHODS

Materials

The zeolite used in this study was supplied by Shenshi Mines Ltd (Zhejiang province, China); its specific gravity is 2.16 t/m³; the hardness is 3-4; the diameter is 3.5–4 mm; the Si/Al ratio is 4.25–5.25; and the specific surface area is 230–320 m²/g. Maintaining the thermal stability temperature of 750 °C, thecation exchange capacity is about 150–180 meq/g. The chemical composition of the zeolites is (in mass): SiO₂ 69.58%, CaO 2.59%, Al₂O₃ 12.2%, MgO 0.13%, Fe₂O₃ 0.87%, Na₂O 2.59%, K₂O 1.13%, and others 10.91%. The cationic surfactant HDTMA was purchased from Aladdin Industrial Corporation, P. R. China. Other chemicals (NH₄Cl, KNO₃, etc.) were purchased from Chengdu Kelong Chemical Reagent Company (Chengdu, P. R. China). Deionized (DI) water (with a resistance of ~18 mΩ-cm) was made with a water purifier (ULUPURE UPT-II-10 T, Chengdu Ultrapure Technology Co., Ltd, Chengdu, P. R. China).

Preparation of SMZ

The raw zeolites were crushed and sieved to 100 mesh (=0.174 mm) in size, sealed in bags for use. To each 600 mL plastic bottle, 100 g of raw zeolite and 500 mL HDTMA solution of a concentration of 1.5, 3.0, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, and 40.0 g/L were mixed in a reciprocal shaker (ZD-85, Jintan Jincheng Guosheng Test Instrument) at 200 rpm and 25 °C for 24 h. Then, the solids were collected by precipitation and washed several times with DI water until no Br⁻ was detected by AgNO₃ solution (Zhan et al. 2011). Finally, the solids were dried at room temperature (24 ± 1 °C).

Sorption experiments

Temperature and pH value would impact the sorption process. In a separate study, it was found that sorption of nitrate on SMZ is an exothermic process, and the effect of temperature is not significant (Zhan et al. 2011). In addition, it has been revealed by several studies that SMZ sorption at a neutral pH exhibited the highest sorption capacity compared to acidic or alkaline pH values (Aghaii et al. 2013). Consequently, tests conducted in this study were carried out under conditions of ambient temperature and neutral pH.

Kinetic batch tests of raw zeolite were conducted by adding 1 g of raw zeolite and 50 mL test solution containing 200 mg/L of either NH₄Cl or KNO₃ into 50 mL centrifuge tube. The tubes were placed in the shaker for reaction at a speed of 200 rpm and a temperature of 25 °C. Samples were collected at each setting time and centrifuged (TCL-16C, Shanghai Anting scientific instrument factory) at 16,000 rpm for 5 minutes, and the supernatant of the samples was stored for analysis.

Sorption isotherm tests for NH₄Cl and nitrate solution were conducted as per the previously reported procedure (similar to kinetic tests) (Li & Bowman 1997; Guan et al. 2010). The NH₄Cl solution was 25, 50, 100, 150, 200, and 250 mg/L and the KNO₃ solution was 25, 60, 100, 140, and 180 mg/L. Orthogonal sorption tests for the 50 mL solution under each of the designed test conditions (see ‘Results and discussion’ section) were conducted with the same procedure.
as the aforementioned kinetic tests with a reaction time of 8 h. The samples were then collected and analyzed with the same procedures as those in kinetic tests. Orthogonal sorption tests were conducted in order to understand the effects of ammonium-N, nitrate-N, and PO4\textsuperscript{3-}P on simultaneous sorption and their corresponding equilibrium capacity.

**Sorption kinetics models and sorption isotherms analysis**

In order to investigate the sorption process of the contaminant on raw zeolite, Lagergren’s first order and pseudo-second order kinetic models were used to fit the experimental date. The Lagergren’s first order kinetic equation is expressed as follows:

\[
\log\left(\frac{q_e}{q_t}\right) = \log\left(\frac{q_e}{C_0}\right) - \frac{k_1}{2.303}t
\]

where \(q_t\) (mg/g) and \(q_e\) (mg/g) are the amounts of contaminant sorbed at time \(t\) and at equilibrium by raw zeolite; \(k_1\) (h\textsuperscript{-1}) is the Lagergren first order rate constant for the sorption process.

The pseudo-second order kinetic equation is expressed as follows:

\[
\frac{t}{q_t} = \frac{t}{K_2q_e^2} + \frac{t}{q_e}
\]

where \(k_2\) (g/mg h) is the pseudo-second rate constant for the sorption process.

The linear form of the Langmuir isotherm model was also used to fit the experimental data:

\[
\frac{C_e}{q_e} = \frac{C_0}{q_{max}} + \frac{1}{q_{max}K_L}
\]

where \(q_e\) (mg/g) is the contaminant sorbed by SMZ; \(C_e\) (mg/g) is the equilibrium concentration of contaminant in the solution; \(q_{max}\) (mg/g) is the maximum monolayer contaminant sorption capacity; and \(K_L\) (L/mg) is the Langmuir sorption equilibrium constant related to the free sorption energy.

**Chemical analysis and quality control**

Ammonium was determined using a UV-1800PC spectrophotometer (Shanghai Mapada Instrument Co., Ltd, China) at 697 nm and the analyzed method was salicylic acid spectrophotometry. Nitrate was analyzed using the UV spectrophotometric method with a detecting wavelength at 220 nm. All tests were conducted in parallel (\(n = 2\)) and the final results were the average of the two samples. The deviation of the duplicate samples was <5% for all the samples.

**Molecular simulation study**

At first, the 3D structure of HDTMA was constructed with the help of MarvinSketch (www.chemaxon.com) and optimized at the molecular mechanical level with the MMFF94 method (Halgren 1996). It was then further optimized in the workspace of Hyperchem (HyperChem Software Hypercube) using the optimized potentials for liquid simulations method (Jorgensen et al. 1996) with the steepest descent algorithm and the MM++ method (Allinger 1977) with the Fletcher-Reeves algorithm (Fletcher & Reeves 1964) consecutively. In addition, HDTMA was optimized at semi-empirical quantum mechanics (SQM) level using the AM1 (Austin Model 1) method (Dewar et al. 1985) with the Polak-Ribiere conjugate gradient algorithm (Grippo & Lucidi 1997) by employing Hyperchem. Consequently, an optimized structure of HDTMA was obtained. The initial conformation of ion pairs was then gained by randomly merging nitrate to the optimized HDTMA in the workspace of Hyperchem. Then, the initial conformation of the ion pair experienced a molecular dynamics (MD) simulation at 300 K for 50 picoseconds (ps) by the aid of Hyperchem. The MD simulation was conducted at the SQM level using the AM1 method (Dewar et al. 1985), and the step size was set to be 0.001 ps.

In order to investigate the interaction energy between HDTMA and nitrate, the last conformation of the ion pair system was optimized by employing MOPAC2012 (Stewart 2012) with the PM6 (Stewart 2007) method. The solvation effect was considered by setting the dielectric constant to 80. Nitrate and HDTMA were also optimized in the same way. Then, the formation heat of nitrate, HDTMA and the ion pair were calculated using MOPAC2012 (Stewart 2012) with the PM6-DH2 (Korth et al. 2009; Korth 2010) method, in which dispersion contribution and hydrogen bond correction were included.

**RESULTS AND DISCUSSION**

**Kinetics and equilibrium tests**

For natural zeolites with or without DI water washing, the time to attain the equilibrium for ammonium sorption was.
The natural zeolite has a good affinity to ammonium but is low to nitrate (anions), indicating that the capacity of natural zeolite for adsorbing nitrate is extremely low and the matrix effects have been taken into consideration (see the details in the Supplementary material, available in the online version of this paper). Natural zeolite washed by DI water has no significant enhancement on removal of contaminant. This may be because the zeolite used in this study had a high purity, and it was hard to improve its sorption behavior and capacity by washing. The values of \( q_e, k_1, k_2 \) and the correlation coefficient of the two kinetic models were determined, as shown in Table 1. It was evident that the correlation coefficient for the Lagergren’s first order kinetic model was relatively low (\( R^2 = 0.701 \), washed), but for the pseudo-second order kinetic model, the correlation coefficients were very high (\( R^2 = 0.999 \), both for unwashed and washed). So the sorption of ammonium onto raw zeolite follows the pseudo-second order kinetic model.

The SMZ appeared to have efficient sorption for ammonium and nitrate (Figure 2). The amount of sorbed contaminants increased with an increase in the initial concentration, while the removal efficiency decreased with an increase in the initial concentration. Similar phenomena have been reported for sorption of hexavalent chromium on granular activated carbon (Ghomshe et al. 2014) and for uptake of cadmium on mixed maghemite–magnetite nanoparticles. At low initial concentrations, there are relatively more sorption sites available, while at higher concentrations, the sorption sites are relatively limited, resulting in the decrease of removal efficiency (Ghomshe et al. 2014).

Table 2 shows that the isotherm experimental results can be fitted with the Langmuir isotherm model (sorption

### Table 1

| Kinetic models’ parameters for sorption of ammonium on raw zeolite |
|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------
| Lagernen’s first order model |
| Pseudo-second order model |
| \( k_1 \) (h\(^{-1}\)) | \( q_{e,cal} \) (mg/g) | \( R^2 \) | \( k_2 \) (g/mg h) | \( q_{e,cal} \) (mg/g) | \( R^2 \) |
| Unwashed | 0.1887 | 1.465 | 0.891 | 1.1379 | 7.527 | 0.999 |
| Washed | 0.1768 | 0.923 | 0.701 | 1.9059 | 7.283 | 0.999 |

### Table 2

| Isothermal parameters for the contaminant of sorption on SMZ |
|---------------------|---------------------|---------------------|---------------------|---------------------|
| Adsorbate | \( q_{max} \) (mg/g) | \( K_L \) (L/mg) | \( R^2 \) | SD of \( q_{max} \) | SD of \( K_L \) |
| Ammonium | 7.241 | 0.083 | 0.978 | 0.0991 | 0.0006 |
| Nitrate | 4.584 | 0.019 | 0.937 | 0.0853 | 0.0015 |
isotherms are presented in the Supplementary material, available in the online version of this paper), which is consistent with previous studies. Based on the Langmuir isotherm model, the predicted maximum monolayer sorption capacity for ammonium and nitrate were found to be 7.241 and 4.584 mg/g, demonstrating that SMZs improved the zeolite’s sorption capacity for nitrate considerably, while still maintaining good sorption properties for ammonium. Similar isothermal parameters have been reported by Li (2003).

**Effect of surfactant concentration and SMZ dosage on sorption**

As shown in Figure 3, the removal efficiency of ammonium decreased with an increase in surfactant concentration. According to previous studies, HDTMA molecules were located on the external surface of zeolites after modification because HDTMA molecules were too large to enter the internal cavities of zeolites (Patdhanagul et al. 2010). HDTMA molecules with a positive charge head group (N terminal) would be attracted to the sorption active sites (which is for cation sorption) on the negative charge surface of zeolite by the Coulomb electrostatic attraction force (Li & Bowman 1997). In general, the external surface area is only 1% of the total surface area of zeolite (She 2013), and the external cation exchange capacity is approximately 10% of the total cation exchange capacity (Bowman 2003). Nevertheless, cationic surfactant modification has little impact on the cation exchange properties of zeolite as there may be no change in the inner cavity structure of the zeolite. Therefore, sorption of ammonium on SMZ achieved a slight decrease compared to raw zeolite. As shown in Figure 3, when ammonium concentration was 200 mg/L, its removal by the SMZs reached above 60% for the SMZs modified with ≤15 g/L surfactant, while the removal by natural zeolite was 70% at the same initial concentration (Figure 1). For ammonium concentrations <100 mg/L, ammonium removal efficiency by SMZs could reach 80% or more. Therefore, compared to raw zeolite, SMZs show a slight reduction in ammonium removal.

For nitrate-N removal, the removal efficiency increased with an increase in HDTMA concentrations up to the HDTMA concentration of 50 g/L (Figure 3). This was due to the increase in positive charges on the surface of SMZs. Further increases in the initial concentration of HDTMA reduced the capacity. Therefore, the surfactant concentration of 50 g/L is a reasonable value for later use.

Comparing Figures 3 and 1, while the ammonium sorption decreased slightly, nitrate sorption increased significantly with SMZs being used. Therefore, the use of SMZs for simultaneous sorption of ammonium and nitrate is feasible.

Figure 4 shows that the removal of the contaminants increased with an increase in the sorbent dosage from 1:50 to 1:10. When the initial ammonium concentration was lower or close to 25 mg/L, the removal for all the SMZ dosages ranged between 95 and 95.5%. However, as the initial ammonium concentration increased, only the tests with a solid/liquid ratio of 1:10 could keep the ammonium removal efficiency steady. The enhancement of contaminant sorption with a higher sorbent dosage can be attributed to the increased surface area of the sorbent and the availability of more active sorption sites. However, the amount of contaminant sorbed per mass of sorbent reduced.
with an increase in the sorbent–liquid ratio. This is because the sorption capacity tended to be stable with the sorption sites being occupied completely (Zhang et al. 2013); when this happens, more sorbent dosage could not make additional contributions to contaminant removal.

Table 3 shows the results of orthogonal experiments. As shown by the range analysis of orthogonal experiments, the factors that affect the ammonium sorption follow the order: contaminant concentration level > contaminant ratio > surfactant dosage. The results for optimization suggested that a contaminant ratio of 35:10:4, contaminant concentration level of 1 and surfactant dosage of 3 g/L could be used to achieve the best ammonium removal (95.2%). The factors that affect the nitrate sorption follow the order: surfactant dosage > contaminant concentration level > contaminant ratio. The optimal condition for nitrate sorption is at the contaminant ratio of 30:5:5, contaminant concentration level of 1 and surfactant dosage of 30 g/L. At these conditions, SMZs showed a significant enhancement on nitrate sorption in the orthogonal experiments; nitrate removal peaked at 81.8% (Table 3).

Significant mutual interference had not been found in sorption of the mixed solution as indicated by sample 8, where nitrate and phosphate removal attained a maximum, and ammonium removal still remained high (93.6%). Results of the orthogonal experiment suggest that the ammonium concentration is the main factor for ammonium sorption, rather than the surfactant dosage, which is consistent with the aforementioned single factor experiments. For nitrate sorption, the surfactant dosage is the most important factor.

![Figure 4](https://iwaponline.com/wst/article-pdf/72/11/1931/465173/wst072111931.pdf)

**Figure 4**: Effect of solid-liquid ratio on sorption as a function of initial concentration of contaminant.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Design and results of orthogonal experimentsa</th>
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<tbody>
<tr>
<td>Test #</td>
<td>Contaminant ratio</td>
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<tr>
<td>1</td>
<td>35:10:4</td>
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<tr>
<td>2</td>
<td>35:10:4</td>
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<td>3</td>
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<td>9</td>
<td>30:5:5</td>
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</table>

*The first four columns are for the experimental design as per three factors and three level orthogonal tests. Column two is the concentration ratio of NH₄⁺-N:NO₃⁻-N:PO₄³⁻-P. The actual contaminant concentration in the test = contaminant ratio × contaminant concentration level (column 3) (e.g. for test #2, NH₄⁺-N = 70 mg/L, NO₃⁻-N = 20 mg/L, PO₄³⁻-P = 8 mg/L). The last three columns are the test results.
Results of SQM MD simulations and interaction energy calculation

As shown in Figure 5(a), the total energy of the ion pair system dropped quickly within several picoseconds and remained at a certain value with a narrow fluctuation over a long period of time (Figure 5(b)). After being simulated for a period of time, conformations of the ion pair were extracted and are shown in Figure 6. From the indicated distance between two nitrogen atoms and the position of a ball-style carbon relative to nitrate, Figure 6 clearly shows that nitrate and HDTMA are trying to find a rational interaction mode by moving, rotating and curving. Figure 5(b) indicates that the ion pair system approaches equilibrium after being simulated for 30 ps at a semi-empirical level using the AM1 method (Dewar et al. 1985). Thus, the conformation of the ion pair after being simulated for 50 ps, the last conformation, was used for investigating interaction further. Figure 7 shows the interaction mode between HDTMA and nitrate and the structure of the optimized ion pair and

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**Figure 5**  | Total energy value of the ion pair system with respect to the simulation time.

**Figure 6**  | Conformations of ion pair after being simulated at semi-empirical level using the AM1 method for 0 (a), 3.900 (b), 4.525 (c), 7.325 (d), 11.850 (e), 14.425 (f), 20.375 (g) and 37.350 (h) picoseconds, respectively. Nitrate was depicted with scaled ball and stick style while HDTMA was represented with stick style. One carbon atom in HDTMA, which was exhibited with ball style, is used as a reference atom to show the position relative to nitrate. The figures in the diagram refer to the distance between two nitrogen atoms which are separately located at two ions. (The chemical formula of HDTMA is C19H42BrN, so we know that two nitrogen atoms represent N of HDTMA and nitrate (two ions), respectively.)
its charging condition. Interaction energy $E_{\text{inter}}$ can be calculated from the heat of formation of ion pair and each of its components according to the following equation:

$$E_{\text{inter}} = \Delta H_f(\text{ion pair}) - \Delta H_f(\text{nitrate}) - \Delta H_f(\text{HDTMA})$$

where $\Delta H_f(\text{ion pair})$, $\Delta H_f(\text{nitrate})$ and $\Delta H_f(\text{HDTMA})$ are corresponding to the heat of formation of ion pair, nitrate and HDTMA, respectively. The heat of formation calculated with the above methods are listed in Table 4. The results of molecular simulations and interaction energy calculation at the SQM level indicate that nitrate sorption on SMZs is a rapid process, and there exists an electrostatic interaction between HDTMA on SMZ and nitrate.

**Environmental implications**

Former research focused on ammonium or nitrate removal by SMZ separately. The present study complements previous studies by determining simultaneous removal of both compounds because they usually coexist in wastewater. This study demonstrates that HDTMA-modified SMZs can simultaneously remove ammonium and nitrate significantly; meanwhile competing with other anions (e.g. phosphate) hardly reduces the removal of nitrate. In addition, the molecular simulation in the study indicates that electrostatic interaction exists between HDTMA sorbed on zeolite and nitrate. The molecular simulation method can be used to study the sorption mechanism of SMZ. Considering the low cost of zeolite and HDTMA, the simple procedure to make SMZs and easy operation, SMZs should have good potential for simultaneous removal of nitrogen in different forms.

**CONCLUSIONS**

The following conclusions can be drawn from this study.

1. Natural zeolite had good affinity for ammonium, but low sorption ability for nitrate, and the HDTMA-modified zeolite had a significant enhancement on nitrate sorption, with a slight decrease in ammonium sorption, but the overall sorption is still good.
2. For SMZ, the sorption process fitted well with the Langmuir isotherm and the predicted maximum monolayer sorption capacity for ammonium and nitrate were found to be 7.241 and 4.584 mg/g. For raw zeolite, the ammonium sorption process followed the pseudo-second order kinetic model.
3. SMZ had a simultaneous sorption of ammonium and nitrate at the low concentration range (<100 mg/L for ammonium and <10 mg/L for nitrate).
4. In the presence of coexisting competing phosphate, the removal efficiency of nitrate is still high.
5. Semi-empirical quantum molecular simulation indicated that electrostatic attraction exists between HDTMA and nitrate.
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Quan Tao and Mu Hu contributed equally to this paper.

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