Simultaneous removal of nitrogen and phosphorus by cetylpyridinium bromide modified zeolite

Chengle Li, Jing Yao, Tian C. Zhang, Wenya Xing, Ying Liang and Mingli Xiang

ABSTRACT

In this study, surfactant modified zeolite-clinoptilolite (SMZ) by CPB (cetylpyridinium bromide) was used for simultaneous removal of ammonium, nitrate and phosphate in synthetic wastewater, and the sorption properties of SMZ were determined and compared with natural zeolite. Results showed that natural clinoptilolite had good affinity for ammonium (8.940 mg/g), but not for nitrate (0.427 mg/g) and phosphate (0.801 mg/g). With the increase of surfactant loading from 5 g/L to 40 g/L, the sorption capacity for nitrate increased from 0.462 mg/g to 4.661 mg/g. When the surfactant loading is 40 g/L, the SMZ has a phosphate adsorption capacity of 2.119 mg/g. The SMZ had a significant enhancement on nitrate and phosphate sorption, could simultaneously remove ammonium, nitrate and phosphate at specific conditions, with removal efficiency up to 85.2%, 83.1% and 56.7%, respectively. Orthogonal experiments showed that ammonium concentration was the most important factor for ammonium sorption on SMZ. Surfactant loading was the major factor for nitrate and phosphate sorption. With the increase of surfactant loading from 5 g/L to 40 g/L, the sorption capacity for nitrate increased from 0.462 mg/g to 4.661 mg/g. When the surfactant loading is 40 g/L, the SMZ has the best phosphate adsorption capacity 2.119 mg/g. Samples were characterized by X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET). Semi-empirical quantum mechanics molecular simulation indicated that electrostatic attraction existed between CPB and dihydrogen phosphate ion. Results indicate that SMZs might have great potential of removing cations and anions simultaneously in the aquatic environment, which is good for eutrophication control and nutrients removal.

Key words | ammonium, cetylpyridinium bromide (CPB), nitrate, phosphate, sorption, surfactant modified zeolite (SMZ)

INTRODUCTION

It is well known that if sewage containing nitrogen (N), phosphorus (P) and other inorganic salts produced by human’s activity enters the natural water without good treatment, it would cause eutrophication or be harmful to human health (Yu et al. 2014). Because both N (e.g. ammonium-N and nitrate-N) and P are valuable nutrients, it is essential to develop an eco-friendly and highly efficient technology to effectively recover them in the aquatic environment. Of all the options available for the removal and recovery of aqueous N and P, sorption is the most effective, flexible, reliable, and environmentally friendly treatment process. Sorption (e.g. adsorption and ion exchange) has less investment and capital costs, simple operation and management, and is applicable to the majority of small- and medium-sized water treatment plants. However, traditional sorbents still have many drawbacks that make them impractical for use in certain settings, including low sorption capacity, strong matrix effects (i.e. low selectivity to P or N), leaching of dopant metals, poor reusability, low specific surface area (i.e. fewer sorption sites), weak mechanical properties, difficulty of recovery, and high cost. Therefore, there is a clear need for the development of new, improved sorbents to recover N and P from waters.

Zeolite is widely used to remove cations (e.g. heavy metals and ammonia) in water (Zhou & Boyd 2014; Deravanesiyan et al. 2015). Zhu et al. (2011) used eight
adsorbents, including zeolite, to remove the ammonium-N (NH$_4^+$-N) from synthetic wastewater. The result shows that the zeolite has the best removal rate of NH$_4^+$-N, because it has a large surface area and adsorption sites (Zheng & Zhang 2011; She 2013). However, natural zeolites have little or no affinity for anions, as they possess permanent negative charges on their structural frameworks (Faghihian & Bowman 2005). Recently, surfactants modified zeolite (SMZ) has been used to increase the capacity of absorbing inorganic anions from wastewater (Zhan et al. 2011; Barczyk et al. 2014; Naghash & Nezamzadeh-Ejhieh 2015). Studies indicate that sorption coefficients of organics increased with the chain length of the cationic surfactant (Lee et al. 1989). For example, cetylpyridinium bromide (CPB), containing 16 carbons, was used to modifying zeolite to sorb anions (e.g. nitrate and phosphate). It is indicated that the maximum monolayer nitrate adsorption capacity for CPB-modified zeolite at 298 K was found to be 9.36 mg/g (Zhan et al. 2011). For P, the adsorption capacity is reach to 0.25 mg/g (Lin et al. 2010). However, to our knowledge, simultaneous removal of N and P by CPB-modified zeolite has not been studied in detail.

This paper discussed the possibility of simultaneous removal of ammonium, nitrate and phosphate by CPB-modified zeolite. The sorption effect and mechanisms have been explored through the analysis of sorption isotherms, orthogonal sorption tests, semi-empirical quantum mechanics molecular simulation, X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET).

### MATERIAL AND METHODS

#### Material

The natural zeolite used in the experiment is clinoptilolite provided by Shenshi Mineral Ltd (Jinyun, Zhejiang, China). The main chemical component of natural zeolite is shown in Table 1. Its Si/Al ratio is 5.02; the aperture is 35–40 nm; the particle size is less than 75 μm; and the thermal decomposition temperature is 750 °C. Other chemicals were purchased from Chengdu Kelong Chemical Reagent Company (Chengdu, Sichuan, China). Deionized (DI) water is made with a water purifier (Ulupure UPT-II-10T, Chengdu Ultrapure Technology Co., Ltd, Chengdu, China). CPB was used as cationic modifier, whose hydrophobic groups is composed of 16 C hydroxyl groups, connected with the hydrophilic groups. Its counter-ions are positively charged when dissolved in water and have a strong adsorption capacity (Guo & Jia 2002).

#### Preparation of CPB-modified zeolite

Crush the natural zeolite with grinder and filter the power zeolite with 100-mesh sieve. Wash the power zeolite with DI water three times in order to remove the soluble material on the surface of the zeolite, and then dry out the zeolite. To each 300-mL polyethylene bottles, mix 50 g natural zeolite and 250 mL CPB solution of a concentration (in g/L) of 5.0, 10.0, 15.0, 20.0, 30.0, and 40.0, respectively, in a Thermostat Oscillator (SHA-2(A), Baita Xinbao Instrument Factory, Changzhou, Jiangsu, China) at 25 °C and 200 rev/min (rpm) for 24 h. Then wash the solids with DI water until Br$^-$ is not detected by AgNO$_3$ solution and dry out in the Electric Oven Blast (DHG-9050A, Shanghai Hongdu Electronic Technology Company, Shanghai, China) at 40 °C for 24 h.

#### Sorption kinetic tests

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 that SMZ sorption at a neutral pH exhibited the highest sorption capacity compared to acidic or alkaline pH values by several studies (Aghaie et al. 2013). Consequently, tests were conducted at ambient temperature and neutral pH. NH$_4$Cl, KNO$_3$ and KH$_2$PO$_4$ solution was prepared as three kinds of synthetic wastewater (200 mg/L of each, separately). Experiments were carried out in glass flasks (total volume 100 mL), which were shaken (in a Thermostat Oscillator) and water-bathed (25 °C). 50 mL synthetic wastewater and 1 g CPB-modified zeolite were added into the flask. The samples at setting time of 5, 10, 20, 30, 45, 60, 120, 300, 600, 960, 1,440 min were collected (there are 11 flasks for one adsorption kinetic curve, 5 mL samples were taken from different time flasks).

<table>
<thead>
<tr>
<th>Chemical component</th>
<th>Mass fraction (%)</th>
<th>Chemical component</th>
<th>Mass fraction (%)</th>
</tr>
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<tbody>
<tr>
<td>SiO$_2$</td>
<td>69.58</td>
<td>K$_2$O</td>
<td>1.13</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
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<td>Fe$_2$O$_3$</td>
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</tr>
<tr>
<td>CaO</td>
<td>2.59</td>
<td>MgO</td>
<td>0.13</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>2.59</td>
<td>Others</td>
<td>10.91</td>
</tr>
</tbody>
</table>

Table 1 | Chemical component of natural zeolite
The zeolites are separated from each sample solution, using centrifuges (TGL-16C, Anke High Tech Limited by Share Ltd, Shenzhen, China) at 16,000 rpm. Then, the supernatants were detected for NH$_4^+$-N, NO$_3^-$-N and H$_2$PO$_4^-$-P.

### Isothermal sorption experiment

Sorption isotherm tests for NH$_4^+$-N, NO$_3^-$-N and H$_2$PO$_4^-$-P were conducted as sorption kinetic tests (only the samples at setting time 480 min were collected). Sorption tests were carried out in glass flasks (total volume 100 mL) filled with 50 mL synthetic wastewater with each concentration shown in Table 2 (only one kind of ions in each bottle) and 1 g zeolite, which were shaken in Thermostatic Oscillator (200 rpm) and water-bathed (25 ºC) for 8 h.

### Coexisting ion experiment

The coexisting ion experiments for ammonia were conducted in 3.74 mmol/L NH$_4$Cl, containing 18.69 mmol/L co-existing ions, which were prepared by dissolving chloride of cations (Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and K$^+$) into DI water, respectively. For phosphate, 1.47 mmol/L KH$_2$PO$_4$ and 7.35 mmol/L potassium salt of forms of anions (Cl$^-$, SO$_4^{2-}$, and NO$_3^-$) were dissolved into DI water, respectively. 1.98 mmol/L KNO$_3$ and 9.9 mmol/L potassium salt of forms of anions (Cl$^-$, SO$_4^{2-}$, and PO$_4^{3-}$) were dissolved into DI water, respectively. All experiments were carried out in 100 mL glass flasks containing 50 mL synthetic wastewater and 1 g 30 g/L CPB-modified zeolite at neutral pH, which were shaken in Thermostatic Oscillator (200 rpm) and water-bathed (25 ºC) for 8 h.

### Orthogonal sorption tests

There are many factors that affect the treatment of N and P mixed synthetic wastewater by CPB-modified zeolite, such as the concentration of CPB modifier, the initial concentration of NH$_4^+$-N, NO$_3^-$-N and H$_2$PO$_4^-$-P, pH, etc. Table 3 shows the experiment conditions used in these orthogonal sorption tests. The orthogonal tests was designed according to the experiments designed by Tao et al. (2015).

### Analytical methods and characterization of zeolite

The concentration of NH$_4^+$-N was determined by HJ536-2009 salicylic acid spectrophotometry (HJ536-2009). The concentration of NO$_3^-$-N was determined by HJ636-2012 alkaline potassium persulfate digestion UV spectrophotometric method (HJ636-2012). The concentration of phosphate is determined by GB11893-89 ammonium molybdate spectrophotometric method (GB11893-89). Surface morphology, surface area, pore size and crystal structure of zeolite was analyzed by XRD and BET. For XRD, X’pert Pro MPD Polycrystalline Diffractometer (Philips Electronic N.V., The Netherlands) was used. Measurement accuracy was 0.001°, and 2θ angle measurement range was from 0° to 160°. GeminiVII 2390t-type Analysis and Determination Instrument (Micromeritics, USA) was used to determine the specific surface area and pore size of zeolite samples before and after modification.

### Sorption isotherms analysis

Langmuir adsorption isotherm was used to fit monolayer model adsorption:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{1}$$

where $C_e$ = the equilibrium concentration of contaminant in the solution, mg/L; $q_e$ = the contaminant sorbed by SMZ, mg/g; $q_m$ = the maximum monolayer contaminant sorption.
capacity, mg/g; \( K_L \) = the Langmuir sorption equilibrium constant.

Freundlich sorption isotherm was used to fit physical adsorption, not limited to monolayer model adsorption:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)
\]

where \( C_e \) = the equilibrium concentration of contaminant in the solution, mg/L; \( q_e \) = the contaminant sorbed by SMZ, mg/g; \( K_F \) and \( n \) = Freundlich sorption equilibrium constant.

### Molecular simulation study

At first, the 3D structure of CPB was constructed with the help of ChemDraw and Chem3D and optimized in the workspace of Hyperchem (Tervo et al. 2006) using OPLS method (Jorgensen et al. 1996) with steepest descent algorithm and MM++ method (Allinger 1977) with Fletcher-Reeves algorithm (Fletcher & Reeves 1964), consecutively. CPB was then further optimized at semi-empirical quantum mechanics (SQM) level using AM1 method (Michael et al. 1985) with Polak-Ribiere conjugate gradient algorithm (Grippo & Lucidi 1997) by employing Hyperchem (Tervo et al. 2006). In addition, CPB experienced a series of molecular dynamics (MD) simulation. It was heated from 0 K to 600 K, run at 600 K, cooled from 600 K to 300 K and run at 300 K. At each stage, the time of MD simulation was set to 50 picoseconds (ps). CHARMM27 (Tabatabaee Ghomshe et al. 2014; Tao et al. 2015) was chosen as the force field. Solvation effect was considered implicitly by setting the scale factor for the dielectric permittivity as 80. Consequently, an optimized structure of CPB was finally obtained.

Dihydrogen phosphate ion (DP) was built with GaussView 3.0 and optimized at semi-empirical quantum mechanics (SQM) level using AM1 method (Michael et al. 1985) with Polak-Ribiere conjugate gradient algorithm (Grippo & Lucidi 1997) by employing Hyperchem (Tervo et al. 2006). The initial conformation of complex, which was composed of CPB and DP, was gained then by randomly merging DP to the optimized CPB in the workspace of Hyperchem (Tervo et al. 2006).

### RESULTS AND DISCUSSION

#### Kinetics and equilibrium tests

Figure 1 shows that natural zeolites, with or without DI water washed, have a good adsorption to ammonia but not to nitrate and phosphate, because of the negative charges on their structural frameworks. The ammonia adsorption capacity is about 8.940 mg/g at setting time 600 min, while phosphate and nitrate adsorption capacity were only 0.801 mg/g and 0.427 mg/g, respectively (Figure 1). The adsorption equilibrium time of natural zeolite to NH\(_4^+\)-N was about 8 h. Natural zeolite washed by DI water had no significantly improvement on the removal efficiency of contaminants, which indicates that the zeolite used in this study had a high purity.

Figure 2 shows the effects of the initial concentration of contaminants on sorption by SMZ. The sorption amount of contaminants increased with the increase of the initial concentration of contaminants, while the removal efficiency decreased. Compared to natural zeolite, the ammonia adsorption capacity of 20 g/L CPB-modified zeolite is about 5.484 mg/g, while phosphate adsorption capacity is 2.425 mg/g (Figure 2), the nitrate adsorption amount of 40 g/L CPB-modified zeolite is 4.661 mg/g.

Figures 3 and 4 and Table 4 show the isotherm experimental results. For ammonium, the isotherm fits Freundlich and Langmuir adsorption model well, for \( R^2 \) of both Freundlich and Langmuir isothermal adsorption model are above 0.9. The constant ‘1/n’ in the Freundlich isothermal adsorption model can reflect the binding capacity between the adsorbent and the adsorbate. In this study, 1/n of CPB modified zeolite was found to be about 0.2 – 0.5, which means that the adsorption process is easy to carry out (Wen et al. 2015). Moreover, the linear correlation of Langmuir isotherm \( R^2 \) is larger than that of Freundlich, indicating that the adsorption process of ammonium by CPB-modified zeolite is basically a monolayer adsorption process. Based on the
Langmuir isotherm model, the predicted maximum ammonia adsorption capacity for 20 g/L CPB-modified zeolite was found to be 6.264 mg/g. As for natural zeolite, the adsorption capacity is 8.940 mg/g (Figure 1) (it does not fit the isothermal adsorption model). After modifying, the adsorption amount of ammonia decreased. It is probably because that CPB molecular blocks the adsorption active sites for ammonia (Li & Bowman 1997).

For phosphate, the adsorption process by CPB-modified zeolite does not fit the Langmuir isotherm adsorption model. The adsorption capacity of P is about 2.43 mg/g when the modifier concentration is 20 g/L (in Figure 2), which can also be seen in Lin’s research (Lin et al. 2010). 1/n of Freundlich isothermal adsorption model is about 1.0, which means the adsorption process of phosphate is mainly linear adsorption.

For nitrate, we can get the same results as for phosphate except that the adsorption process is much easier to carry out because the 1/n of Freundlich isothermal adsorption model is about 0.2–0.6. The maximum monolayer nitrate...
adsorption capacity for CPB-modified zeolite was found to be 2.72 mg/g in Table 4 when the concentration of modifier is 30 g/L, less than 9.36 mg/L (Zhan et al. 2011), which may related to the loading amount of CPB modifier. Thus, from Figure 2, the sorption capacity was found to be 4.66 mg/g when the concentration of modifier is 40 g/L. SMZs have a better affinity for nitrate than for H$_2$PO$_4$-P because the $K_L$ value for nitrate is higher than that for phosphate. As for natural zeolite, the adsorption amount for both phosphate and nitrate do not fit the isothermal adsorption model. The phosphate and nitrate adsorption capacity were only 0.801 mg/g and 0.427 mg/g, respectively (Figure 1). It is demonstrated that SMZs can remarkably improve the adsorption capacity for phosphate and nitrate.

Effect of surfactant concentration and SMZ dosage on sorption

Figure 5 shows the removal efficiency of ammonium by CPB modified zeolite decreased with the increase of the concentration of CPB modifier. According to previous studies, surfactants molecules are located on the surface of the zeolite, without changing the inner cavity structure of the zeolite because the molecules are too large to enter the internal cavities of zeolite (Patdhanagul et al. 2010). The surfactant molecules cover 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), leading to the lower adsorption efficiency of ammonium compared with the natural zeolite in Figure 1. As shown in Figure 5, when the concentration of initial ammonium was 200 mg/L, removal efficiency by the SMZs reached above 50% for the SMZs modified with ≤15 g/L surfactant, while the removal by natural zeolite was 80% at the same initial concentration (Figure 1). Compared with HDTMA-modified zeolite, CPB-modified zeolite has low adsorption capacity to sorb ammonium (Tao et al. 2015), which may be because CPB molecular has a planar structure, and HDTMA molecular has a perspective structure. CPB molecular will cover more pore and pore crossing, blocking ammonia getting into the zeolite.

For phosphate, the removal rate increased with the concentration of CPB from 5 to 40 g/L and reached to 28% when the initial concentration of phosphate is 60 mg/L (actions amount from 0.092 mg/g to 0.849 mg/g), which is basically the same as the previous study (Lin et al. 2010). This was due to the increase in positive charges on the surface of SMZs. The adsorption efficiency of phosphate has a rapid increase with the concentration of CPB increased from 10 to 20 g/L, which may be because the monolayer of the modified zeolite change into bimolecular.

For nitrate, the removal efficiency by CPB-modified zeolite increased with the increase of the concentration of CPB modifier. When the concentration of nitrate in solution was 20 mg/L and the concentration of modifier was 40 g/L, the removal efficiency reached 80%. After modifying, zeolite get
the capacity of adsorbing phosphate and nitrate. Therefore, the use of SMZs on simultaneous sorption of ammonium phosphate and nitrate is feasible.

Figure 6 shows that the removal of the contaminants increased with an increase in the sorbent dosage from 1 to 5 g (i.e. the water to modified zeolite ration changed from 1:50 to 1:10). As expected, all the adsorption capacities of contaminants by SMZs decreased when the sorbent dosage increased, because of the increase in the available adsorption site. For ammonium, however, the sorption capacities ranged between 2.22 mg/g to 2.42 mg/g when the SMZs dosage was 1 g. That is because the sorption capacity tended to be stable with the sorption sites being occupied completely (Zhang et al. 2013). There is a balance in the solution between ammonium and active adsorption sites.

**Results of coexisting ions effects experiments**

The adsorption capacity of ammonia was slightly influenced by Ca$^{2+}$ and Mg$^{2+}$, as shown in Table 5. However, adsorption capacity was significantly affected by Na$^+$ and K$^+$. Na$^+$ and K$^+$ can decrease the adsorption capacity from 2.055 mg/g to 1.578 mg/g and 0.811 mg/g, respectively. This trend was probably caused by the Na$^+$ and K$^+$ competing with the NH$_4^+$ for the available ion-exchange sites on the surface of SMZ and hindered the diffusion of NH$_4^+$ in the pores (Huang et al. 2014a, 2014b). This result also confirmed that ammonia was adsorbed through the ion-exchange mechanism.

For phosphate and nitrate adsorption, Table 5 shows that the anions mentioned above had no or slight effect on the adsorption capacity of SMZ. Results indicated that chloride and sulfate ions has little competitive effect with phosphate and nitrate. There are also little competitive effect between phosphate and nitrate.

**Results of orthogonal experiments**

Table 6 shows the results of orthogonal experiments. Based on Table 6, the factors that affect the ammonium sorption follow the order: initial ammonium concentration > CPB modifier concentration > initial phosphate concentration > initial nitrate concentration. The factors that affect the nitrate sorption follow the order: CPB modifier concentration > initial ammonium concentration > initial phosphate concentration > initial nitrate concentration. The factors that affect the phosphate sorption follow the order: CPB modifier concentration > initial phosphate concentration > initial nitrate concentration > initial ammonium concentration. Results of the orthogonal experiment suggest that the ammonium concentration is the main factor for ammonium sorption, which is consistent with the aforementioned single factor experiments. For nitrate and phosphate sorption, the surfactant modifier concentration is the most important factor.

**Results of characterization**

The specific surface area of natural zeolites and CPB modified zeolites was determined by a nitrogen physical adsorption apparatus. The specific surface area is 7.6219 m$^2$/g and 4.9647 m$^2$/g (Table 7), respectively, for natural zeolite and CPB-modified zeolite. The specific surface area become smaller after modifying because the CPB molecular jams some channels. Figure 7 shows that the BET adsorption–desorption isotherm fits well to III-type

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**Table 4 | CPB modified zeolite adsorption isothermal constants**

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Modifier concentration (g/L)</th>
<th>Langmuir</th>
<th>Freundlich</th>
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<tr>
<td></td>
<td>Ke</td>
<td>qm</td>
<td>R^2</td>
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<tr>
<td>Ammonium</td>
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<td>0.029</td>
<td>5.667</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.037</td>
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</tr>
<tr>
<td></td>
<td>40</td>
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<td>3.516</td>
</tr>
<tr>
<td>Phosphate</td>
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<td>0.0033</td>
<td>3.581</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.0023</td>
<td>66.756</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.0022</td>
<td>74.769</td>
</tr>
<tr>
<td>Nitrate</td>
<td>20</td>
<td>0.023</td>
<td>2.992</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.087</td>
<td>2.724</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.017</td>
<td>6.789</td>
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</table>
isotherm (Xin & Luo 2009). It means that the most pores of natural zeolite and SMZ is macropore (>50 nm).

Figure 8 shows XRD phase analysis of natural zeolite, CPB modified zeolite before and after sorption of ammonium, nitrate and phosphate. Compared the pattern of natural zeolite with that of CPB modified zeolite, they have no obvious differences. It is because that the CPB molecules are too big to enter into the pores of zeolites as mentioned before. The CPB modified zeolites show a large fluctuation in the range of 27.5–35.5° which means that the process of ion exchange and adsorption takes place.
within this range. The patterns of CPB modified zeolite after adsorbing nitrate and phosphate is basically the same, which means the oxygenate ions in the solution formed a bilayer adsorption with the CPB molecules supported on the zeolite surface.

Table 5 | Effect of coexisting ions on adsorption by SMZ

<table>
<thead>
<tr>
<th>Ion type</th>
<th>Qₑ (mg/g)</th>
<th>Ion type</th>
<th>Qₑ (mg/g)</th>
<th>Ion type</th>
<th>Qₑ (mg/g)</th>
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<tr>
<td>NH₄⁺</td>
<td>2.055</td>
<td>NO₃⁻</td>
<td>0.988</td>
<td>PO₄³⁻</td>
<td>1.268</td>
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<tr>
<td>NH₄⁺ + Ca²⁺</td>
<td>2.096</td>
<td>NO₃⁻ + Cl⁻</td>
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<td>PO₄³⁻ + Cl⁻</td>
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<tr>
<td>NH₄⁺ + Mg²⁺</td>
<td>2.237</td>
<td>NO₃⁻ + SO₄²⁻</td>
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<tr>
<td>NH₄⁺ + Na⁺</td>
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<tr>
<td>NH₄⁺ + K⁺</td>
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Table 6 | The result of orthogonal experiments

<table>
<thead>
<tr>
<th>Tests</th>
<th>A*</th>
<th>B*</th>
<th>C*</th>
<th>D*</th>
<th>NH₄⁻-N sorption amount (mg/g)</th>
<th>NO₃⁻-N sorption amount (mg/g)</th>
<th>H₃PO₄-P sorption amount mg/g</th>
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<td>1</td>
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<td>100</td>
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<td>9</td>
<td>150</td>
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<td>5</td>
<td>5.939</td>
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</tbody>
</table>

*Initial concentration (mg/L) of ammonium (A), nitrate (B), phosphate (C) and CPB (D).

Table 7 | Pore structure parameters of adsorbent

| Zeolite            | BET specific surface area (m²/g) | Pore size (nm) |
|--------------------|-----------------------------------|----------------|---------------|
| Natural zeolite    | 7.6219                            | 24.6137        |
| CPB-modified zeolite| 4.9647                           | 33.5893        |

Figure 7 | BET adsorption–desorption isotherm.
Results of SQM MD simulations and interaction energy calculation

A molecular dynamics (MD) simulation at 300 K for 50 ps was conducted on the initial conformation of the complex by the aid of Hyperchem. The simulation was at SQM level using AM1 method and the step size was set to 0.001 ps. Figure 9 shows that the total energy of the complex dropped dramatically within several ps and kept at certain value with a narrow fluctuation in a long period of time. Conformations of the complex being simulated for a period of time were extracted. As is demonstrated in Figure 8, the distance between CPB and DP and the orientation of DP to CPB were changing. It was clearly shown that CPB and DP were trying to find a rational interaction mode by moving and rotation.

In order to investigate the interaction between CPB and DP, the last conformation of the complex was optimized by employing Hyperchem with AM1 method. CPB and DP were also optimized with the same way. Binding affinity $E_{BA}$ was calculated according to Equation (3):

$$E_{BA} = E_{CPB-DP} - E_{CPB} - E_{DP}$$  \hspace{1cm} (3)

where $E_{CPB-DP}$, $E_{CPB}$, and $E_{DP}$ are corresponding the total energy of complex, CPB as well as DP, respectively. Their

Table 8 | Binding affinity and total energy of complex and its components (kcal·mol^{-1})

<table>
<thead>
<tr>
<th>$E_{CPB-DP}$</th>
<th>$E_{CPB}$</th>
<th>$E_{DP}$</th>
<th>$E_{BA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-6415.1531</td>
<td>-5670.3220</td>
<td>-733.1046</td>
<td>-11.7265</td>
</tr>
</tbody>
</table>
total energies calculated with methods mentioned above are listed in Table 8. It is indicated from Figure 9 that the complex composed of CPB and DP approximately approached to an equilibrium after being simulated for 20 ps at SQM level using AM1 method. Thus, the conformation of the complex after being simulated for 50 ps, the last conformation, was used for investigating interaction further. It was optimized at SQM level using AM1 method with Polak-Ribiere conjugate gradient algorithm. Its charging condition is exhibited in Figure 10, which shows that there existed a direct interaction between the most positive hydrogen atom on CPB and the most negative oxygen atom on DP ion. Results of simulation indicated that the distance between these two atoms was 2.060 angstrom. There must be a strong electrostatic interaction between CPB and DP ion.

CONCLUSION

The following can be concluded from this study:

1. Natural zeolite is an attractive material for ammonium removal (the adsorption capacity was about 8.940 mg/g at an ammonium initial concentration of 200 mg/L). CPB-modified zeolite had a slight decrease in ammonium sorption (about 4.21 mg/g at an ammonium initial concentration of 200 mg/L, when the concentration of modifier is 20 g/L).

2. Natural zeolite cannot remove nitrate and phosphate from water.

3. Ca$^{2+}$ and Mg$^{2+}$ had no or slight influence in ammonia adsorption of SMZ, while Na$^{+}$ and K$^{+}$ decreased the ammonia adsorption of SMZ. Chloride and sulfate ions has little competitive effect with phosphate and nitrate. There are also little competitive effect between phosphate and nitrate.

4. SMZ had a good simultaneous sorption capacity of ammonium, nitrate and phosphate (with 150 mg/L for ammonium, 30 mg/L for nitrate and 10 mg/L for phosphate, the removal efficiency is 82.24%, 83.07%, 56.70%, respectively).

5. Semi-empirical quantum molecular simulation indicated that electrostatic attraction exists between CPB and dihydrogen phosphate ion.

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