Adsorption Performance on Sediment Nutrients by Different Proportions of Zeolite and Shale Ceramsite (ZSC)

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Abstract

Sediment capping is an effective way to control internal pollution sources in eutrophic water. However, there is a lack of research on absorption of sediment nutrients – especially both nitrogen and phosphorus – by materials that are low-cost to be utilized in engineering. In this study, zeolite and shale ceramsite (ZSC) were selected to explore their adsorption performance on sediment nutrients. And the morphology and microstructure of ZSC were characterized by scanning electron microscope (SEM), X-ray fluorescence (XRF), Fourier transform infrared (FTIR) and X-ray diffraction (XRD). Results showed that the optimal proportion of ZSC on sediment nutrients adsorption was 2:1. The removal rates of sediment nutrients did not increase with the increasing dosage of ZSC, and optimal dosage of ZSC was 5 g with 5 g sediments. And the adsorption performance by the ZSC on sediment nutrients was mainly on total phosphorus (TP), total nitrogen (TN) and ammonia nitrogen (NH$_4^+$-N). The adsorption mechanism analysis found that ZSC adsorbed sediment nitrogen and phosphorus mainly by physical adsorption and nonspecific chemisorptions. These results indicated that ZSC can be further used to control and reduce sediment nutrients in eutrophic water.

Keywords: zeolite, shale ceramsite, sediment capping, adsorption, sediment nutrients

Introduction

Freshwater eutrophication is a serious environmental problem worldwide [1, 2]. It adversely affects aquatic ecosystems and adversely impacts related goods and services, human health and economic activity. External pollution sources and internal pollution sources are the main causes for eutrophication. External pollution sources such as sewage, industrial discharge and agricultural runoff contain lots of nutrients [3]. And there are many widely accepted methods to control external nutrients into waters [4]. Internal pollution sources and enriched sediment can release nutrients to water, which aggravates water deterioration [5]. Accordingly, more attention should be paid to controlling and reducing internal nutrients in sediment.

Generally, the ex-situ sediment dredging is considered an effective restoration strategy to reduce nutrients, heavy metals and special pollutants such as
arsenic and selenium from sediment permanently [6-8]. However, dredging effects varying by season and high cost, and increasing the risk of spreading contaminants made it more strictly apply this method [9, 10]. On the contrary, there are many in-situ approaches employed in sediment treatment such as sediment capping [3, 11], phytoremediation [12, 13], and chemical reagents [14, 15]. Among these, sediment capping is an effective and low-cost way that places adsorption materials over sediment. And selection of adsorption materials is crucial to this method for the reason that the adsorption materials can absorb nutrients as well as stabilize sediment [16, 17].

Up to now, there has been much research of materials on the N or P absorption. The nitrogen adsorbents are mainly zeolite [18] and modified zeolite [11]. The phosphorus adsorbents are modified maifanite [19], modified zeolite [20], modified local soils [5] and so on. But several issues remain: (1) lack of studies on materials absorption of both nitrogen and phosphorus; (2) the adsorption effect of modified materials is better, but it is still in the stage of laboratory research, and the production technology is not mature enough to carry out large-scale production. Therefore, it is of great scientific significance and engineering application to study the adsorption effect of both nitrogen and phosphorus on natural materials.

Zeolite, composed of silica, aluminum and oxygen, is distinguished by its systematic structure that consists of plenty of channel and pore cavities [21]. As a common nitrogen adsorbent, zeolite is unique in its porous structure and enhanced adsorption, ion-exchange, and catalytic properties. Nuernberg et al. [22] found that the zeolites successfully adsorbed the ammonia released from poultry litter. Zeolite was effective in eliminating ammonia from aqueous solution [23], is widespread in terrestrial environments and is a low-cost mineral. Shale ceramsite is traditional environmental material with high metal (Ca, Fe, Al or Mg) content. It displays excellent phosphorus removal properties for its chemical adsorption, precipitation or biological adsorption mechanisms [24, 25]. However, to our knowledge, few studies have concerned the adsorption performance on sediment N and P by different proportions of zeolite and shale ceramsite (ZSC).

Hence, we prepared and tested ZSC as in-situ physical adsorption materials to remove sediment nutrients. The main aims are to (1) explore the optimal proportion and dosage of ZSC to achieve the best adsorption effect on nutrients simultaneously; (2) describe the structural properties of ZSC after adsorption; and (3) analyze the adsorption mechanisms.

### Materials and Methods

#### Sediment Sampling

The sediments selected for this study were collected from the Huangxiaohu River in Wuhan City, China (114°28′E, 30°62′N). Surface sediments (0-10 cm) were sampled using a Peterson grab sampler. The samples were transported to the laboratory under 4°C. Then the samples were dried in oven at 55°C to constant weight and sieved with a stand 100-mesh sieve for further experiments. The physical properties and chemical compositions of surface sediment are shown in Table 1.

#### Zeolite and Shale Ceramsite

Zeolite (2-4 mm in diameter) was purchased from Runjia Environmental Protection Co., Ltd. and shale ceramsite (2-4 mm in diameter) was purchased from Xinjiang Material Co., Ltd. Zeolite and shale ceramsite were rinsed with tap water 3 times, then washed by ultrapure water 3 times, followed by drying at 105±5°C. The physical properties of Zeolite and shale ceramsite are shown in Table 2.

#### Dynamic Adsorption Experiments

**Exploring the optimal proportion of ZSC**

Different weight ratios of 5 g ZSC (zeolite and shale ceramsite: 1:4, 1:2, 1:1, 2:1, 4:1) and 5 g sediment were added to Erlenmeyer flasks containing 250 mL 0.02 mol/L KCl solution with pH at 7.0, respectively. The Erlenmeyer flasks were sealed and shaken in a thermostat shaker (20±2°C) at 200 rpm for 0.5 h, 1 h, 2 h, 4 h, 6 h, 8 h, 12 h, 16 h, and 24 h, respectively. After the adsorption process, a 0.45 μm membrane was used to filter the mixture to obtain filtrate. Then total nitrogen (TN), ammonia nitrogen (NH₄⁺N), total phosphorus (TP) and chemical oxygen demand (COD) were determined and the removal rates were calculated to determine the optimal proportion as:

\[
R_t = \frac{C_{t,0} - C_{t,1}}{C_{t,0}} \times 100\%
\]

...where \( R_t \) is the removal rate at time \( t \), \( C_{t,0} \) is the concentration of sediment without ZSC at time \( t \), and \( C_{t,1} \) is the concentration of sediment with ZSC at time \( t \) [26]. Each ratio of ZSC was done with three replicates.

### Table 1. Physical properties and chemical compositions of surface sediment.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Water content (%)</th>
<th>ORP (mv)</th>
<th>pH</th>
<th>Organic matter (%)</th>
<th>TP (mg/g)</th>
<th>TN (mg/g)</th>
<th>NH₄⁺-N (mg/g)</th>
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<tr>
<td>Content</td>
<td>265.23</td>
<td>217.2</td>
<td>7.03</td>
<td>18.59</td>
<td>4.76</td>
<td>4.97</td>
<td>0.12</td>
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</table>
Different weights of the optimal proportion of ZSC (2 g, 5 g, 8 g, 10 g, 12 g, 15 g) and 5 g sediment were added to Erlenmeyer flasks containing 250 mL 0.02 mol/L KCl solution with pH at 7.0, respectively. The flasks were sealed and shaken in a thermostatic shaker (20±2°C) at 200 rpm for 24 h. After the adsorption process, TN, NH₄⁺-N, TP and COD of filtrate were determined and the removal rates were calculated to determine the optimal dosage.

**Static Adsorption Tests**

The optimal dosage of ZSC and 5 g sediment samples were added to Erlenmeyer flasks containing 250 mL 0.02 mol/L KCl solution with pH at 7.0. Then the sealed flasks were kept in dark condition at 20±2°C for 3 d, 6 d, 9 d, 12 d, 15 d and 18 d. After the adsorption process, filtrate was obtained with a 0.45 μm membrane. Then TN, NH₄⁺-N, TP and COD were determined and the removal rates were calculated. Testing of each time was done with three replicates.

**Analytical Methods**

TN, NH₄⁺-N, TP and COD of filtrate were analyzed following standard procedures [27]. TN was determined by alkaline potassium persulfate digestion-UV spectrophotometric method. Nessler’s reagent spectrophotometry was used to determine NH₄⁺-N. TP was determined by ammonium molybdate spectrophotometric method. And The COD was analyzed using a spectrophotometer (DRB 200, Hach, USA). All statistical analyses were performed using SPSS IBM Statistics version 23 (Illinois, USA). TN, NH₄⁺-N, TP and COD of dynamic adsorption experiments assessed the differences (P<0.05) by using one-way ANOVA, followed by the Tukey post hoc tests to identify homogenous groups.

The overview morphologies of ZSC samples were acquired by SEM (SU8010, Japan). The chemical...
analyses of ZSC samples were performed using an XRF (AXIOSmAX, Netherlands) instrument. XRD patterns were obtained by way of rotation anode high-power X-ray diffraction (D8-FOCUS, Germany). FTIR (Nicolet6700, USA) spectra were collected using a Nicolet iS50 FTIR spectrometer.

**Results and Discussion**

**Characterizations of ZSC**

**SEM**

The morphology and microstructure of zeolite and shale ceramsite were observed by SEM. As shown in Fig. 1a) and Fig. 1b), zeolite composed of small dense particles had voids, and shale ceramsite displayed a loose and porous microstructure.

**XRF**

The chemical compositions of zeolite and shale ceramsite were determined by XRF. Both zeolite and shale ceramsite were primarily a mixture of Si, Al, K, Fe, and Mg oxides, of which SiO₂ was the main composition, accounting for above 67% (Table 3).

**XRD**

Peak positions and characteristics of zeolite and shale ceramsite were shown with XRD patterns ranging from 5° to 90° (Fig. 3a and b). The most abundant mineral compounds in zeolite were quartz (JCPDS card no. 33-1161) [28], cristobalite (JCPDS card no. 11-695) [28], calcium aluminum oxide hydrate (JCPDS card no. 24-217) [29] and gismondine (JCPDS card no. 39-1373) [30]. The main mineral compound in zeolite was quartz (JCPDS card no. 33-1161) [28].

**FTIR**

Characteristic functional groups of substrate materials can be distinguished by FTIR [31]. The broad peak at 3130-3450 cm⁻¹ and 1620-1640 cm⁻¹, corresponding to OH vibrations, appeared for zeolite and shale ceramsite. There was a band of around 465 cm⁻¹ of zeolite and shale ceramsite, which

<table>
<thead>
<tr>
<th>Materials</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>TiO₂</th>
<th>CaO</th>
<th>Na₂O</th>
<th>P₂O₅</th>
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<tr>
<td>Zeolite</td>
<td>76.48</td>
<td>20.67</td>
<td>1.02</td>
<td>1.07</td>
<td>0.21</td>
<td>0.05</td>
<td>0.19</td>
<td>0.23</td>
<td>0.01</td>
</tr>
<tr>
<td>Shale ceramsite</td>
<td>67.11</td>
<td>15.50</td>
<td>5.87</td>
<td>4.22</td>
<td>1.55</td>
<td>0.98</td>
<td>0.41</td>
<td>0.08</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table 3. XRF analyses of zeolite and shale ceramsite (wt. %).

Fig. 2. XRD patterns of zeolite a) and c) and shale ceramsite b) and d) before a) and b) and after c) and d) the adsorption process.
belonged to the vibration of Si-O-Fe. A broad band centered on 694 cm$^{-1}$ assigned to Si-O-Al vibrations was also present for zeolite. The additional band of zeolite at about 800 cm$^{-1}$ due to carbonate (feldspar) was shown (Fig. 3).

Sediment Nutrient Adsorption by ZSC in Dynamic Adsorption Experiments

Optimal Proportion of ZSC on Sediment Nutrient Adsorption

To explore the optimal proportion of ZSC on sediment nutrient adsorption, experiments were performed with different proportions of ZSC from 0.5 h to 24 h. The results are presented in Fig. 4. The removal rates of TP by 2:1 of ZSC were higher from 1 h to 24 h except for 12 h, and there were significant differences between 2:1 and others at 2 h, 4 h, 6 h and 8 h, respectively (2 h: $F = 294.01, P<0.05$; 4 h: $F = 43.19, P<0.05$; 6 h: $F = 117.17, P<0.05$; 8 h: $F = 32.62, P<0.05$) (Fig. 4a). For TN, the removal rates of by 2:1 of ZSC were much higher from 2 h to 24 h than other proportions except for 6 h (4 h: $F = 16.84, P<0.05$; 8 h: $F = 66.97, P<0.05$; 12 h: $F = 35.87, P<0.05$; 16 h: $F = 27.87, P<0.05$; 24 h: $F = 63.98, P<0.05$) (Fig. 4b). After 4 h, the removal rates of NH$_4^+$-N by 2:1 of ZSC were significantly greater than others (6 h: $F = 63.42, P<0.05$; 8 h: $F = 36.44, P<0.05$; 12 h: $F = 99.31, P<0.05$; 16 h: $F = 227.73, P<0.05$; 24 h: $F = 14.49, P<0.05$) (Fig. 4c). However, there was no certain trend among the removal rates of COD by different proportions of ZSC (Fig. 4d). Therefore, the optimal proportion of ZSC on sediment nutrient adsorption was 2:1.

Optimal Dosage of ZSC on Sediment Nutrient Adsorption

To select the optimal dosage of ZSC, 6 different weights of 2:1 of ZSC were done to compare the removal rates of TN, NH$_4^+$-N, TP and COD (Fig. 5). The highest removal rates of TP were found at 5 g and 15 g respectively ($F = 27.90, P<0.05$) (Fig. 5a). The removal rates of TN increased first and then decreased with ZSC dosage increasing, and there was no significant difference among the dosage of 5 g, 8 g and 10 g ($F = 1.16, P>0.05$) (Fig. 5b). For NH$_4^+$-N, the dosage of 5 g, 8 g and 15 g showed better removal efficiency ($F = 54.83, P<0.05$) (Fig. 5c). But there was no significant difference among the different dosages of ZSC for removal of COD ($F = 1.64, P>0.05$) (Fig. 5d). Thus, given the removal efficiency and cost-efficiency, the dosage of ZSC 5 g was adopted as optimal for sediment nutrient adsorption.

Static Adsorption Tests

To imitate the adsorption sediment nutrients under in-situ conditions, static experiments were carried out with 5 g sediment and 5 g 2:1 of ZSC from 0 to 18 d. The removal rates of TP increased with time and achieved peak value at 18 d, which was similar to TN (except for the peak value at 15 d). The removal rates of NH$_4^+$-N increased slowly and the maximum removal rate was 7.99% at 18 d. However, the removal efficiency of ZSC on COD decreased and the removal rate was -12.88% at 18 d (Fig. 6). Hence, adsorption performance by the ZSC on sediment nutrients was mainly on TP, TN and NH$_4^+$-N.

Characterizations of ZSC After Adsorption

SEM

As in Fig. 1, more substances emerged for zeolite and shale ceramsite after the adsorption process, which may be evidence for adsorption performance on sediment nutrients by ZSC.
Fig. 4. Effects of different proportions of ZSC on adsorption of sediment nutrients.

Fig. 5. Effects of different dosages of ZSC on adsorption of sediment nutrients.
After comparison of the XRD patterns before and after the adsorption process shown in Fig. 2, the mineral compositions of zeolite and shale ceramsite had no obvious change.

FTIR

There were no significant changes for FTIR spectra of ZSC between the beginning and end of the adsorption process (Fig. 3). The peaks of zeolite at 1033.60 cm$^{-1}$ disappeared while the peak at 3448.79 cm$^{-1}$ shifted to 3453.65 cm$^{-1}$ after the adsorption process (Fig. 3a). The peaks of shale ceramsite at 3446.19 cm$^{-1}$, 1057.33 cm$^{-1}$, 777.30 cm$^{-1}$ and 453.16 cm$^{-1}$ shifted to 3449.50 cm$^{-1}$, 1061.90 cm$^{-1}$, 783.88 cm$^{-1}$ and 458.64 cm$^{-1}$, respectively. And the peaks at 3766.01 cm$^{-1}$ and 1636.74 cm$^{-1}$ disappeared (Fig. 3b).

Hence, ZSC can perform physical adsorption for nitrogen and phosphorus in sediments mainly for its large specific surface area and good porosity. Meanwhile there were iron and aluminum oxide and other chemical components in ZSC, which may lead to nonspecific chemisorptions. The mineral composition and chemical composition of ZSC found no significant change after the adsorption process, indicating that nonspecific chemisorptions did not change the chemical structure of ZSC. But specific reaction process and mechanism need further analysis.

Conclusions

This study explored removal rates of sediment nutrients by different proportions and dosages of ZSC in dynamic adsorption experiments and imitated the adsorption sediment nutrients under in-situ conditions. Then the adsorption mechanism was analyzed. Results showed that 2:1 of ZSC was the optimal proportion for sediment nutrient adsorption. Given the removal efficiency and cost-efficiency the dosage of ZSC same to sediments can have better removal efficiency. There was good adsorption performance on TP, TN and NH$_4^+$-N by ZSC, except for COD through physical adsorption and nonspecific chemisorptions. Therefore, ZSC can be applied as promising capping materials in eutrophic water. And the combination of ZSC and other ecological methods may be a new way and more beneficial to ecological restoration.

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References