Effect of magnetic iron-zirconium modified zeolite on the different phosphorus forms in river sediment under aerobic and anoxic conditions

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\textbf{ABSTRACT}

In this study, a magnetic iron-zirconium modified zeolite (FeZrMZ) was synthesized. Through sediment culture experiments, the influence of the addition of modified materials on the migration and transformation of phosphorus in river sediments was investigated. The results showed that the modified zeolite could not only effectively reduce the phosphorus concentration in the overlying water, but also significantly reduce the phosphorus concentration in the pore water of sediments. The addition of modified zeolite makes the unstable weakly adsorbed phosphorus (NH\textsubscript{4}Cl-P) and redox phosphorus (BD-P) transform into the more stable metal oxide-bound phosphorus (NaOH-P) and very stable residual phosphorus (Res-P). The four types of bioavailable phosphorus (BAP), including water-soluble phosphorus (WSP), readily desorbable phosphorus (RDP), algae-available phosphorus (AAP), and NaHCO\textsubscript{3} extractable phosphorus (Olsen-P). Under anoxic conditions, they were reduced by 53.5\%, 14.1\%, 23.8\%, and 49.9\% respectively. Under aerobic conditions, they were reduced by 23.2\%, 16.6\%, 32.1\%, and 50.0\%. The addition of magnetic iron-zirconium modified zeolite could clearly reduce the release potential of phosphorus in sediment, and it could be recovered through the action of an external magnetic field, so it could be used as an effective sediment modifier to control the sediment release of phosphorus.

\textbf{Key words:} magnetic iron-zirconium modified zeolite, most variable P forms, phosphorus migration, sediment

\textbf{HIGHLIGHTS}

\begin{itemize}
  \item Synthesize and characterize FeZrMZ, which has a good magnetic separation ability.
  \item FeZrMZ can effectively reduce the concentration of phosphorus in overlying water and interstitial water.
  \item FeZrMZ can convert unstable phosphorus in sediments into stable phosphorus.
\end{itemize}

\textbf{GRAPHICAL ABSTRACT}

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INTRODUCTION

The eutrophication of lakes has become a hotspot of scientific research into the water environment. The main cause of eutrophication of lakes is the accumulation of excessive phosphorus (Xiang & Zhou 2011; Stow & Cha 2013; Mucci et al. 2018). The accumulation of phosphorus is divided into two types: external source and internal source. The input of external source phosphorus is often caused by human activities such as agriculture, animal husbandry and industrial sewage discharge (Tu et al. 2019). The input of external phosphorus can be reduced or eliminated by controlling and regulating human behavior (Hörppila et al. 2017). Endogenous phosphorus is often caused by the external conditions of lake sediment unstable phosphorus release, so it is difficult to control the effects of human. When exogenous phosphorus is effectively controlled, controlling the release of endogenous phosphorus is of great significance to the restoration of eutrophic lakes (Li et al. 2019; Wang et al. 2017a, 2017b, 2017c).

Various methods have been developed to control the release of endogenous phosphorus at home and abroad, including sediment dredging (Chen et al. 2018), aeration oxygen supply (Tammeorg et al. 2017), microbial treatment (Wang & Pei 2013), aluminum salt passivation (Mucci et al. 2018), in situ treatment of calcium oxide (Xu et al. 2018), addition of nitrate (Yamada et al. 2012), inactivation of phosphorus by coagulant (aluminum, iron or calcium based chemicals) (Mucci et al. 2018; Li et al. 2020), and modified attapulgite (Yin et al. 2016). In recent years, the use of in situ modification technology to control the release of phosphorus in sediments has attracted widespread attention at home and abroad. In situ modification technology is to directly add modified materials to the sediments, improve the passivation ability of phosphorus to control the release of phosphorus, or modified material is added to the surface of the sediment, so that it forms a protective layer at the sediment–water interface, to achieve the purpose of reducing the release of phosphorus from sediments (Lin et al. 2019). Compared with traditional sediment dredging, this treatment process is relatively simple and easy to operate, it can reduce the secondary pollution produced in the treatment process, has a less adverse impact on the environment, and can significantly reduce the phosphorus release from the sediment and improve the phosphorus fixation capacity of the sediment.

Choosing suitable modified materials is the key to successfully control the release of endogenous phosphorus. In this regard, some modifiers have been proposed to control the release of phosphorus from sediment at home and abroad, including lanthanum-modified zeolite (Wang et al. 2017a, 2017b, 2017c), lanthanum-modified bentonite (Wang et al. 2017a, 2017b, 2017c), thermally treated calcium-rich sepiolite (Yin et al. 2013), drinking water residue (Wang et al. 2017a, 2017b, 2017c), calcium silicate hydrate (Li et al. 2017), zirconium-modified zeolite (Yang et al. 2014, 2015; Fan et al. 2017), or zirconium-modified bentonite (Lin et al. 2016). Each modified material has its own advantages and disadvantages. In recent years, the zirconium-based modified materials have attracted increasing attention due to their wide sources, easy access and excellent passivation effect on phosphorus, they are harmless to the environment and have good stability. Therefore, the study of the passivation effect of zirconium-based modified materials on phosphorus in sediment will help to control phosphorus release from sediment. The release of phosphorus in sediment is affected by dissolved oxygen. When the sediment is in a shallow position and the dissolved oxygen in water is sufficient, an oxidation layer will be formed on the surface of the sediment, and the phosphorus in the oxidation layer is difficult to release because it is adsorbed by hydroxyl iron oxide (Chen et al. 2016; Meng et al. 2018). When the sediment is at a deeper position, the water is insufficiently oxygenated and is usually in an anoxic state. Due to the reduction and dissolution of iron oxyhydroxide and the hydrolysis of calcium and phosphorus by microorganisms, phosphorus in the sediment is released into the water (Zhang et al. 2018; Gao et al. 2020; McDowell et al. 2020). Previous studies have found that zirconium-based modified zeolite and zirconium-based modified bentonite have an effect on the unstable weakly adsorbed phosphorus (NH<P>4Cl-P) and redox state phosphorus (BD-P) to the more stable metal oxide-bound phosphorus (NaOH-P) and very stable residual phosphorus (Res-P), have a significant conversion effect, and significantly reduce the content of biologically available phosphorus (BAP) (Fan et al. 2017; Soliman et al. 2017).

Although the zirconium-based modified passivator has a good effect on the treatment of phosphorus in the sediment, it also has the defect that it is difficult to recover when it is added to the sediment. Part of the phosphorus adsorbed by the zirconium-based passivation agent still exists as potentially active phosphorus, which may be re-released into the pore water and overlying water of the sediment when the external environment changes (Cavalcante et al. 2018; Hu et al. 2020). Therefore, it is necessary to separate and recover zirconium-based modified materials from sediments. In this paper, magnetic iron zirconium modified zeolite was prepared, which can be adsorbed under the action of external magnetic field, so as to realize the recovery of traditional modified materials in sediment. In addition, the adsorption of phosphorus on the overlying water and the pore water of the sediment by the magnetic iron-zirconium modified zeolite was investigated through a sediment
incubation experiment. After cultivation, the sequential extraction method was used to analyze the occurrence characteristics of the modified materials on the phosphorus in sediments and the influence on bioavailable phosphorus, which provided theoretical basis and technical support for the control of phosphorus pollution in river sediments.

MATERIALS AND METHODS

Experimental materials
The sediment used in this study was from Tuo River, Suzhou City, Anhui Province, China. The total length of Tuo River is 243 km, with a drainage area of 2,983 km². It flows in from the northwest of Suzhou City and flows out from the southeast, passing through the urban residential areas and commercial entertainment areas. The annual average discharge is 3.52–72.10 m³ s⁻¹, and the annual average water level elevation is +14.73–26.56 m.

The collected sediment is screened and dried before passing through the screen for standby. The particle size of the sediment and zeolite passing through the screen is 0.075 mm. The chemical reagents used in the experiment were purchased from Sinopharm Chemical Reagent Co., Ltd, all of which were analytical pure reagents (AR).

Preparation and characterization of FeZrMZ
For FeZrMZ preparation 5 g ZrOCl₂·8H₂O, 11.657 g FeCl₃·6H₂O, 5.99 g FeSO₄·7H₂O, and 10 g zeolite weighed into a 1,000 ml conical flask, 100 ml deionized water was added to the flask, and then the solution was heated on a constant temperature (70 °C) on a magnetic stirrer for 1.5 h. After that the pH of the solution was adjusted to 10 with 1 mol L⁻¹ NaOH. Magnetic stirring was carried out at 70 °C for 1 h before centrifugation, the solid material obtained by centrifugation was washed eight times with deionized water, and then dried in an oven at 105 °C. Finally, the prepared FeZrMZ solid was crushed and ground, passed through a sieve with a diameter of 0.075 mm, and then stored in a sealed bag for standby.

The X-ray diffractometer (XRD, model Empyrean, manufactured by PANalytical, The Netherlands, Cu target, Kα ray source, λ = 0.15406 nm) was used to analyze the mineral composition of the original and iron-zirconium modified zeolite. The X-ray photoelectron spectrum (XPS, model Nexsa, and ThermoFisher manufacturer) of the modified material was measured by a spectrometer equipped with a monochromatic aluminum Kα source (1,486.6 electron volts). The surface morphology of the original and iron-zirconium-modified zeolite was observed using a JSM-7800 scanning electron microscope.

Sediment incubation experiment
Through sediment release simulation experiments, the influence of modified materials on the migration and transformation of phosphorus in sediments was investigated. In total, eight cylindrical devices with a diameter of 6 cm and a height of 30 cm were used in the incubation experiment. Four incubation schemes were set up in two replicates: sediment with FeZrMZ (as treatments) and without it (as controls) under aerobic and anoxic conditions. Next, 50 g air-dried sediment were weighed into four incubator chambers and 5 g of FeZrMZ was added and mixed evenly in the treatment chambers. The simulated overlying water containing 1 mmol L⁻¹ NaHCO₃, and CaCl₂ and 10 mmol L⁻¹ NaCl with pH of 7.5 was added to the incubation apparatus to form a covering layer of 26 cm. For simulating anoxic conditions, an appropriate amount of Na₂SO₃ was added into the incubator chambers to remove the dissolved oxygen (DO) in the overlying water (Kim et al. 2003), then the chambers were air tied. The incubator was placed at room temperature for 41 days, during the simulated sediment release period, the pH, DO and soluble reactive phosphorus (SRP) in the upper water were measured on the 7th, 14th, 21st, 31st and 41st days respectively.

After incubation, centrifugation was used to obtain the pore water in the sediment and the concentration of SRP was measured. The obtained sediment samples were dried and crushed, after grinding, and passed through a screen with a diameter of 0.075 mm and stored in a sealed bag for standby.

Continuous extraction of phosphorus form sediment
A continuous chemical extraction method was used to determine weakly adsorbed phosphorus (NH₄Cl-P), redox phosphorus (BD-P), metal oxide-bound phosphorus (NaOH-P), hydrochloric acid extracted phosphorus (HCl-P) and residual phosphorus (Res-P) in sediment (Pote et al. 1996; Haygarth & Sharpley 2000; McDowell et al. 2001; Wang et al. 2016). The extraction procedure is shown in supplementary Figure 1. Next, 1 g of sediment was weighed and put into a centrifuge tube, 25 ml NH₄Cl solution, NaHCO₃/Na₂S₂O₄ mixture solution, NaOH solution, HCl solution and NaOH solution were added
successively for the reaction. After the reaction, the centrifuge tube was taken out for centrifugation, and then the concentration of phosphorus in the supernatant was determined.

**Extraction of bioavailable phosphorus (BAP)**

Following the method reported previously in the literature, the bioavailable phosphorus was extracted (Lu et al. 2016). For determination of water-soluble phosphorus (WSP): 0.2 g sediment was weighed into a centrifuge tube, 20 ml of deionized water was added, and the tube put into a constant temperature water bath oscillator for 2 h (25 °C and 200 r min⁻¹). For determination of readily desorbable phosphorus (RDP): 0.2 g sediment was weighed into a centrifuge tube, 20 ml of 0.01 mol L⁻¹ CaCl₂ was added, and the tube put into a constant temperature water bath oscillator for 2 h (25 °C and 200 r min⁻¹). For determination of algae-available phosphorus (AAP): 0.2 g sediment was weighed into a centrifuge tube, 20 ml of 0.1 mol L⁻¹ NaOH was added, and the tube put into a constant temperature water bath oscillator to react for 4 h (25 °C and 200 r min⁻¹). For determination of NaHCO₃ extractable phosphorus (Olsen-P): 0.2 g of sediment was weighed in a centrifuge tube, 20 ml of 0.5 mol L⁻¹ NaHCO₃ was added, and the tube put into a constant temperature water bath oscillator to react for 0.5 h (25 °C and 200 r min⁻¹). After the above steps, the supernatant was centrifuged and filtered through a 0.45 μm filter membrane. The phosphorus concentration was determined using a UV-Vis spectrophotometer at the wavelength of 700 nm.

**Data processing**

DO in overlying water was measured with a portable dissolved oxygen meter (DO 80) produced by WIGGENS company, and pH value of overlying water was measured using a portable pH meter (ST20T-B) produced by OHAUS (Shanghai, China) (Yu et al. 2020). The collected overlying water and pore water were first filtered through a 0.45 μm filter membrane, and then SRP in the overlying water and pore water was determined (Wang et al. 2017a, 2017b, 2017c).

In the overlying water, DO was measured with a portable dissolved oxygen meter (DO 80, WIGGENS, Germany), and pH was measured using a portable pH meter (ST20T-B, OHAUS, Shanghai, China). The collected overlying and sediment pore water were first filtered through a 0.45 μm filter membrane, and then SRP was determined.

According to the SRP concentration in the pore and the overlying water in the sediment incubation experiment, the phosphorus diffusion flux \( F, \text{mg (m² d)}^{-1} \) at the sediment-water interface was calculated based on Fick’s first law (Equation (1)) (Yu et al. 2017):

\[
F = -D_s \frac{\partial c}{\partial Z} |_{Z=0}
\]

where \( \emptyset \) is the porosity of the sediment. In this experiment, \( \emptyset \) is taken as 0.75; \( D_s \) is the phosphorus diffusion coefficient in the sediment (cm² s⁻¹), which can be determined according to Equations (2) and (3); \( \partial c/\partial Z|_{Z=0} \) is the concentration gradient of phosphorus at the sediment-water interface [mg (L cm⁻¹)]:

\[
D_s = \emptyset DO \quad \emptyset < 0.7
\]

\[
D_s = \emptyset^2 DO \quad \emptyset > 0.7
\]

where \( DO \) is the diffusion coefficient of ions in an ideal diluted solution (cm² s⁻¹), in this study \( DO \) was taken as \( 7.34 \times 10^{-6} \text{ cm² s}^{-1} \) (Yu et al. 2017).

**RESULTS AND DISCUSSION**

**Characterization of FeZrMZ**

In order to verify the magnetic separation ability of FeZrMZ, the original zeolite or FeZrMZ was mixed with ultrapure water, and then a magnet was used to separate the mixture. The result is shown in supplementary Figure 2, the mixed solution containing FeZrMZ (right side) quickly became clear, and the solids in the FeZrMZ mixed solution gather on the side of the tube adjacent to the magnet. However, the mixed solution containing zeolite (left side) was turbid, and the solid in the suspension settled on the bottom of the beaker after a period of standing. This showed that FeZrMZ has a good magnetic separation effect under the action of an external magnetic field.
The XRD patterns of natural zeolite and FeZrMZ are shown in Figure 1. The mineral compositions of natural zeolite and FeZrMZ are similar, but the peak strength of FeZrMZ is lower than that of natural zeolite, which indicates that the crystal form of FeZrMZ is not as good as that of natural zeolite. The morphology of natural zeolite and FeZrMZ was studied by scanning electron microscopy (SEM). Figure 2(a) represents the electronic scanning image of natural zeolite, and Figure 2(b) represents the electronic scanning image of FeZrMZ, the surface of natural zeolite presented a flaky structure, while the surface of FeZrMZ was composed of aggregated particles. This difference in appearance well supported the loading of iron and zirconium on the zeolite surface after modification. Further XPS measurement was performed to confirm the presence of elements on the zeolite surface and FeZrMZ, and the results are shown in Figure 3. The wide-scan electron energy spectrum showed that Al, Si, Fe, C, O and Na are present in the original zeolite and FeZrMZ. The results showed that the percentage of iron and zirconium in FeZrMZ increased significantly, indicating that iron and zirconium were successfully loaded onto the surface of FeZrMZ. The presence of the core level peaks of Zr 3p and Zr 3d in the XPS wide-scan spectrum confirmed the presence of zirconium in FeZrMZ. The atomic percentages (%) of elements in zeolites and FeZrMZ determined by XPS are given in Table 1.

**Effect of adding FeZrMZ on overlying water environment**

Figure 4(a) shows the change in DO in the overlying water during the sediment incubation process. It can be seen that, in the anoxic experimental group, the DO of the control group and the added chambers showed a slow upward trend under anoxic conditions, which may be due to a small amount of oxygen entering the incubator at sampling events. Compared with the control group, the DO of added chambers did not change significantly, which indicated that FeZrMZ had no obvious
effect on DO. The DO value was less than 0.7 mg L\(^{-1}\) during the whole incubation process, which was always at a low level, meeting the requirements of anoxic incubation experiments (Wang et al. 2017a, 2017b, 2017c). In the aerobic experimental group, with the development of the incubation experiment, the content of DO increased first, then decreased and then increased, and finally returned to the level of DO in overlying water at the beginning of incubation. Under aerobic conditions, the addition of FeZrMZ did not change significantly compared with the control group, indicating that the addition of FeZrMZ under aerobic conditions had no obvious effect on DO. The DO value was about 5 mg L\(^{-1}\) in the process of 41 days of the sediment incubation process, which met the requirements of the aerobic incubation experiment.

Figure 4(b) shows the change in pH in the overlying water during the sediment incubation process. In the anoxic group, the incubation process showed a slight downward trend of pH, and in the aerobic group, the overall process showed a slight upward trend. After 35 days of incubation, the pH of all experimental groups remained unchanged. During the whole process, the pH of the aerobic experiment group was maintained at 8.0–8.5, and the pH of the anoxic experiment group was maintained at 7.8–8.7. The pH was slightly alkaline in both anoxic and aerobic groups, and treatment group had no significant effect on pH compared with the control group. The above results show that the addition of FeZrMZ has no adverse effect on the environment.

**Effect of FeZrMZ addition on SRP in overlying water**

Figure 5(a) shows the change of SRP in overlying water during sediment incubation. During the 41 days incubation process, the concentration of SRP increased from 0 to 0.026 mg L\(^{-1}\) in the aerobic control group and from 0 to 0.156 mg L\(^{-1}\) in the anoxic control group. The results showed that the phosphorus in the sediment will release into the overlying water under aerobic and anoxic conditions, and the phosphorus release was more favorable under the anoxic conditions. Under aerobic and anoxic conditions, adding FeZrMZ will significantly reduce the concentration of SRP in the overlying water, and the effect was more obvious under anoxic conditions. Figure 5(b) shows the removal efficiency of phosphorus in overlying water by adding FeZrMZ. It can be seen from the figure that the removal efficiency of SRP by FeZrMZ increased with
When the incubation experiment lasted for 41 days, the removal efficiency of SRP by FeZrMZ reached 73.5% under aerobic conditions, and 95.5% under anoxic conditions.

The release of phosphorus in the sediment into the overlying water was affected by many factors such as DO, redox potential, temperature, pH, physical disturbance and biological disturbance (Piao et al. 2015). These processes led to the release of phosphorus in the sediment to the water through the dissolution of metal oxides/hydroxides, the mineralization of organic matter, and the exchange of competitive hydroxyl anions (OH⁻) with ligands (Zhan et al. 2015). Affected by pH, under acidic conditions, iron-aluminum-bound phosphorus may be released from the sediment, while under alkaline conditions, calcium-bound phosphorus may be released, but both are difficult to release under neutral conditions (Zhang et al. 2018). It can be seen from Figure 4(b) that the pH of the aerobic experimental group was always slightly higher than neutral during the entire cultivation process. Therefore, there was a certain amount of OH⁻ in the overlying water. The exchange of phosphate and OH⁻ ligand in the iron/aluminum complex is the main way to cause the release of phosphate in the sediment to the overlying water, the release of iron-bound phosphorus is mainly controlled by the oxidation-reduction potential (Kiani et al. 2020). Under aerobic conditions, the iron in the sediment mainly exists in the form of Fe³⁺, and the phosphorus will be adsorbed by iron hydroxide and is in a relatively stable state, under anoxic conditions. Fe³⁺ will be reduced to Fe²⁺, which will lead to the dissolution of iron hydroxide (Lin et al. 2019). As a result, phosphorus and iron are released simultaneously. Combined with Figure 4(a), it can be seen that DO in the anoxic group is always at a low level. Low DO concentration will cause iron hydroxide to dissolve, resulting in phosphorus release along with iron hydroxide dissolution, which is one of the reasons for the change in SRP concentration in the overlying water. Conversely, it can be found from Figure 4(b) that the pH of the overlying water in the anoxic experimental group is always in a weak alkaline state. Therefore, the exchange of phosphate and OH⁻ ligand in the iron/aluminum complex is another reason for phosphorus release from sediment to overlying water. The above results showed that the release of phosphorus in the sediment was mainly affected by pH under aerobic conditions, and was mainly affected by pH and DO under anoxic conditions, but addition of FeZrMZ could greatly inhibit the release of phosphorus from sediment to the overlying water.
Effect of FeZrMZ addition on SRP in pore water

Pore water is an important medium for phosphorus exchange at the sediment–water interface. The process of phosphorus release from sediment to the overlying water is that phosphorus in sediment is released into pore water first, and then released from pore water to the overlying water (Li et al. 2017). Therefore, revealing the effect of FeZrMZ addition on SRP in pore water is helpful to understand the mechanism of controlling phosphorus release from sediment. After 41 days of the sediment incubation experiment, the concentration of SRP in the pore water was analyzed. Results are shown in Table 2, the concentration of SRP in the pore water of the control group and the treatment group was 0.084 mg L\(^{-1}\) and 0.017 mg L\(^{-1}\) respectively under aerobic conditions; the concentration of SRP in pore water in the FeZrMZ addition group decreased by 79.8%. The concentration of SRP in pore water was 0.250 mg L\(^{-1}\) and 0.021 mg L\(^{-1}\) in the control group and the treatment group, respectively under anoxic conditions, and the concentration of SRP in pore water decreased by 91.6%. Compared with aerobic and anoxic control groups, the concentration of SRP in pore water under anoxic conditions was higher than that under aerobic conditions, which indicated that phosphorus in sediment was more easily released into pore water under anoxic conditions. This can be explained as follows: it is generally believed that the redox potential under anoxic conditions is lower than that under aerobic conditions, and the lower redox potential will reduce part of BD-P (redox phosphorus) and release some BD-P from the sediment, resulting in SRP in pore water under anoxic conditions higher than that under aerobic conditions (Tammeorg et al. 2017). The above results showed that FeZrMZ has excellent adsorption capacity for SRP in the pore water under both aerobic and anoxic conditions, which is the same as that of FeZrMZ for SRP removal from overlying water. Therefore, adding the modified zeolite to the sediment can effectively reduce the concentration of SRP in the pore water, thus reducing the risk of SRP release from the pore water to the overlying water, and finally reducing the SRP concentration in the overlying water.

**Effect of FeZrMZ addition on SRP diffusion flux at sediment–water interface**

According to the SRP content in the overlying water and pore water after the 41 days incubation period, the diffusion flux of SRP at the sediment–water interface was calculated using Eqn (1) (Yu et al. 2017). The results showed that the diffusion flux of SRP to overlying water was 0.180 mg (m\(^2\) d\(^{-1}\)) and 0.035 mg (m\(^2\) d\(^{-1}\)) in the control group and the treatment group, respectively. The addition of FeZrMZ reduced the diffusion flux of SRP by 81.7%. Under anoxic conditions, the diffusion flux of SRP to overlying water was 0.289 mg (m\(^2\) d\(^{-1}\)) and 0.044 mg (m\(^2\) d\(^{-1}\)) in control group and treatment group, respectively. The addition of FeZrMZ reduced the diffusion flux of SRP by 84.8%. This shows that adding FeZrMZ can significantly inhibit the release of SRP from pore water to overlying water. There are two processes for phosphorus release from sediment to overlying water. First, phosphorus in sediment is released to the pore water by sediment supplement, and then phosphorus in pore water is released to overlying water by phosphorus concentration difference between pore water and overlying water (Yu et al. 2017). The diffusion flux of SRP under anoxic conditions is higher than that under aerobic conditions, which is consistent with the release of SRP in overlying water and pore water. Combined with the above results, it can be concluded that the addition of FeZrMZ inhibits the release of phosphorus from sediment to pore water, and the decrease in phosphorus concentration in pore water makes the difference between pore water and overlying water narrow, thus reducing phosphorus release from pore water to overlying water, and finally significantly reducing SRP diffusion flux.

**Effect of FeZrMZ addition on phosphorus forms in sediment**

Different forms of phosphorus in sediment have different release potential. Understanding the effect of adding modified zeolite on the occurrence of phosphorus in sediment is helpful to clarify the mechanism of controlling sediment release by adding

<table>
<thead>
<tr>
<th>Experience group</th>
<th>SRP concentration (mg L(^{-1}))</th>
<th>Removal rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control group (aerobic)</td>
<td>0.084</td>
<td></td>
</tr>
<tr>
<td>Treatment group (aerobic)</td>
<td>0.017</td>
<td>79.8%</td>
</tr>
<tr>
<td>Control group (anoxic)</td>
<td>0.250</td>
<td></td>
</tr>
<tr>
<td>Treatment group (anoxic)</td>
<td>0.021</td>
<td>91.6%</td>
</tr>
</tbody>
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*Table 2 | Effects of adding FeZrMZ on SRP content and removal rate in pore water

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modified zeolite (Piao et al. 2015). Figure 6 shows the changes of various forms of phosphorus contents in sediment before and after the addition of modified zeolite. It can be seen from Figure 6(a), 6(b) and 6(d) that NH₄Cl-P, BD-P and HCl-P are significantly reduced under aerobic and anoxic conditions. Adding FeZrMZ under aerobic and anoxic conditions reduced NH₄Cl-P by 55.7 and 57%, BD-P by 31.8% and 22.3%, and HCl-P by 88.2% and 94.8%. In contrast, it can be seen from Figure 6(c) and 6(e) that both NaOH-P and Res-P increased significantly. When FeZrMZ was added under aerobic and anoxic conditions, NaOH-P increased by 25.0% and 23.0%, and Res-P by 7.2 times and 7.3 times respectively. The ratio of various forms of phosphorus to the total extractable phosphorus before and after the addition of modified zeolite was further calculated, and the results are shown in Figure 7. It can be seen from the figure that the addition of FeZrMZ had a significant effect on the phosphorus form of the sediment, resulting in the decrease of the proportion of NH₄Cl-P, BD-P, and HCl-P, and an increase in the proportion of NaOH-P and Res-P. This showed that the addition of modified zeolite can transform NH₄Cl-P, BD-P, and HCl-P into NaOH-P and Res-P.

NH₄Cl-P refers to the weakly adsorbed phosphorus in the sediment, and mainly refers to the phosphate adsorbed by the mineral particles in the sediment, it is unstable and easily released into the water body when the external environment changes (Wang et al. 2013). BD-P refers to redox sensitive phosphorus, and mainly refers to phosphorus combined with...
iron manganese oxide, which is easily released when the redox potential is low (Wang et al. 2013; Moura et al. 2020). NaOH-P refers to the phosphorus adsorbed on the surface of aluminum oxide and inside iron oxide, which is easily released into water at high pH. HCl-P refers to phosphorus fixed by calcium and magnesium minerals, which can easily enter water under low pH environments (Hrenovic et al. 2008). Res-P refers to residual phosphorus, which is less affected by the environment and has stable properties (Wang et al. 2016). NH₄Cl-P and BD-P are called potentially active phosphorus, and are unstable and easily affected by the environment. The properties of NaOH-P and HCl-P are relatively stable, are less affected by the environment, and are not easy to release. Res-P is extremely stable and difficult to release. Under anoxic and aerobic conditions, the content of potentially active phosphorus in sediment decreased by 33.1% and 27.2% after adding FeZrMZ, possibly because NH₄Cl-P and BD-P are transformed into more stable NaOH-P and Res-P. It should be noted that the mechanism of the modified zeolites reduced the content of potential active phosphorus. The potential active phosphorus in the pore water were absorbed and transformed by the modified zeolite, resulting in the decrease in concentration. The sediment will supply the potential active phosphorus to the pore water, so that the phosphorus content in the sediment and pore water will be reduced. It can be seen from Figure 7 that the content of HCl-P had been significantly reduced, the content of Res-P significantly increased, and the content of NaOH-P had not changed much, only slightly increased. This indicated a significant transition from HCl-P to Res-P. When FeZrMZ is added under aerobic and anoxic conditions, the content of Res-P accounts for 49 and 50% respectively, and the stable form of phosphorus in the sediment accounts for half, which is difficult to release again (Wang et al. 2017a, 2017b, 2017c). This indicates that the addition of FeZrMZ increases the stability of phosphorus in the sediment. Although most of the phosphorus in the sediment is in a relatively stable state after the addition of modified zeolite, there is still some potential active phosphorus in the sediment (Lin et al. 2016). This phosphorus is active and easy to be released into the pore/overlaying water, and the NaOH-P and HCl-P in the sediment still have the potential to be released from the sediment when the external environment changes. Therefore, it is necessary to separate and adsorb the saturated modified zeolite in time. FeZrMZ has the characteristics for magnetic separation, and can be separated from the sediment under an external magnetic field, therefore solving this problem. The above results show that FeZrMZ can significantly control the release of phosphorus from sediment, and has the characteristics of magnetic separation, and is therefore is a more promising material for controlling phosphorus release in sediment.

**Effect of FeZrMZ addition on BAP in sediment**

Bioavailable phosphorus refers to phosphorus that can be directly or indirectly utilized by algae. Understanding the influence of modified zeolite on bioavailable phosphorus is also a way to evaluate the control effect of modified zeolite on phosphorus in sediment. Figure 8 shows the content of each component of bioavailable phosphorus, and the order of each component content is AAP > Olsen-P > WSP > RDP. AAP is the best estimate of bioavailable phosphorus required for algae growth,
and the content of AAP is related to the content of iron aluminum oxide (Wang et al. 2013). As shown in Figure 8(a), after adding FeZrMZ, the content of AAP decreased by 32.1% and 23.8% under aerobic and anoxic conditions, respectively. This indicates that the addition of modified zeolite can significantly reduce the content of AAP. WSP is easy to release phosphorus and is the best estimate of phosphorus available immediately in sediment (Cassagne et al. 2000). Figure 8(b) shows the effect of the addition of modified zeolite on WSP. After adding FeZrMZ, the content of WSP decreased by 23.2% and 53.5% under aerobic and anoxic conditions, respectively. This shows that the addition of modified zeolite can effectively reduce the content of WSP. RDP is considered an available phosphorus in algae, and its content is related to the content of NH₄Cl-P (Wang et al. 2013). Figure 8(c) shows the effect of modified zeolite on RDP before and after addition. The content of RDP in sediment is less, and the addition of modified zeolite also makes the content of RDP decrease to some extent. After adding FeZrMZ, the content of RDP decreased by 16.6% and 14.1% under aerobic and anoxic conditions, respectively. Olsen-P is a quantitative indicator of BAP, including some inorganic phosphorus forms (such as NH₄Cl-P, BD-P and NaOH-P) and active HCl-P (Li et al. 2011). Figure 8(d) shows the change in the Olsen-P content before and after the addition of the modified material. After adding FeZrMZ, the content of Olsen-P decreased by 50.0% and 49.9% under aerobic and anoxic conditions. This shows that the addition of modified zeolite can significantly reduce the content of Olsen-P. In contrast to the control group, except for AAP, the contents of the other three kinds of bioavailable phosphorus were higher in anoxic condition than in aerobic condition, which indicated that the release of WSP, RDP and Olsen-P was more favorable under anoxic conditions. In contrast, aerobic conditions are more conducive to the release of AAP. The addition of modified zeolite has the largest removal content for AAP and the highest removal rate for Olsen-P. The above results show that FeZrMZ can significantly reduce the content of BAP in sediment under anoxic and aerobic conditions, which can effectively reduce the possibility of eutrophication.

**CONCLUSION**

Through the above research, the main conclusions are as follows:

1. The FeZrMZ modified material prepared with zeolite as raw material is easy to be separated by magnetic separation and recovered from sediment, which has a significant effect on controlling phosphorus release from river sediment.
2. FeZrMZ can effectively reduce the concentration of SRP in overlying water and sediment pore water in 41 days of sediment incubation experiment. The release rate of phosphorus is accelerated under anoxic conditions, but the release rate of phosphorus can be effectively inhibited by adding modified zeolite.

3. The addition of FeZrMZ can transform unstable potentially active phosphorus (NH₄Cl-P and BD-P) and HCl-P to more stable NaOH-P and Res-P, and effectively reduce the content of AAP, Olsen-P, WSP and RDP in the sediment.

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

**REFERENCES**


Wang, C., Gao, S., Pei, Y. & Zhao, Y. 2013 Use of drinking water treatment residuals to control the internal phosphorus loading from lake sediments: laboratory scale investigation. *Chemical Engineering Journal* 225, 93–99.


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