Releasing control of nitrogen and phosphorus from contaminated sediment covered with aluminum-zirconium modified zeolite

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Abstract. In this paper, aluminum and zirconium based metal compounds were used to modify natural zeolite to produce Al-Zr modified zeolite (AZMZ). The adsorption performance, micro morphology and releasing control effect of AZMZ on nitrogen and phosphorus from sediment were tested. Test results show that the adsorption performance of natural zeolites on ammonia nitrogen and phosphate in water was significantly improved after Al-Zr modification. The adsorption model is chemical adsorption, and follows the quasi second-order kinetic equation and Langmuir model. The saturated adsorption capacity of 0.5 to 1.0 mm size of AZMZ for ammonia nitrogen and phosphate in water is 8.40 mg/g and 3.10 mg/g respectively. AZMZ has the potential to be used as in-situ covering materials to control the release of nitrogen and phosphorus from sediment. The average release rate was reduced by the increasing thickness of AZMZ. When the covering thickness of AZMZ reaches 0.5 cm, the releasing rate of nitrogen and phosphorus in the sediment can be effectively controlled. When the AZMZ thickness reaches 1.0 cm, the releasing reduction rate of nitrogen and phosphorus in the sediment are 89.1% and 75.3% respectively.

1. Introduction

Presently, there are mainly two types of technologies for treatment of the contaminated sediment: in-situ and ex-situ treatment methods. The in-situ treatment technology treatment of the contaminated sediment in-situ and take measures to prevent the pollutants from sediment into the water body. Which means cut off the pollution path of the internal pollution source; the ex-situ treatment technology is to excavate the polluted sediment and transport it to other places for treatment, that is, to transfer the internal pollution source of the water body, so as to prevent the pollution of the water body. The widely used in-situ treatment technologies mainly include covering (masking), curing, oxidation, water diversion, physical washing, air jet and electrodynamic repair [1]. Ex-situ treatment technology mainly includes dredging, ex-situ washing, vitrification, etc. As a kind of in-situ treatment technology of sediment, covering (masking) has a very obvious effect on remediation of polluted sediment, and the project cost is low. It can effectively prevent the secondary pollution caused by the pollutants in the sediment from entering the water body, and it is suitable for both organic and inorganic types of sediment.

The research and application of controlling the release of nitrogen and phosphorus from sediment are mainly based on the formation of insoluble precipitates of aluminum salt, calcium salt, iron salt and PO₄³⁻ released into water in the covering materials, so as to inhibit the release of PO₄³⁻ [2]. The
Research on the control of nitrogen and phosphorus release from sediment by covering method began in the 1980s, and there have been successful precedents of using slag [3,4], gypsum [5,6], lime [7], sodium aluminate [8] to inhibit the release of nitrogen and phosphorus from sediment in rivers, lakes and offshore bays. In this study, Al-Zr modified zeolite materials were prepared and characterized, and the static release of nitrogen and phosphorus in sediment under the cover of AZMZ was studied.

2. Materials and methods

2.1. Sediment

The sediment used in the study is from the Maozhou river dredging ship in Shenzhen. The sediment is generally black, with impurities such as snail, shell, masonry, domestic waste and so on. The mobility is relatively strong. After the sediment is collected and transported back to the laboratory, the impurities are removed through a 5 mm sieve with an aperture, and then it is sealed and stored in a plastic bucket under shading to prevent its natural degradation and loss of water in the mud.

See Table 1 for the main physical and chemical indexes of sediment and Table 2 for the content of heavy metal elements. According to the data in the table, according to the national soil environmental quality standard (GB15918-1995), the content of heavy metal cadmium in the sediment exceeds the national level III standard, and cadmium pollution exists in the sediment. The content of other heavy metals is within the standard.

| Component | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | K₂O | Na₂O |
|-----------|------|-------|-------|-----|-----|-----|------|
| Content % | 68~70| 13~14 | 1~1.8 | 1.8~2.2 | 0.9~1.4 | 1.6~3.9 | 0.6~1.2 |

The natural zeolite used in the study is produced in Jiajinkou Town, Gongyi City, Henan Province, and its main components are SiO₂ and Al₂O₃ (see Table 3). The particle size of zeolite is 0.5-1mm and 2-4mm, the apparent density is 2.16g/cm³, the bulk density is 1.21g/cm³ and 1.11g/cm³, and the void ratio is 44% and 50%, respectively. As shown in Figure 1.

2.2. Test method

(1) Modification treatment of natural zeolite

In this experiment, 0.5-1mm and 2-4mm natural zeolite were used as raw materials, which were modified by anhydrous aluminum trichloride (aluminum salt) and zirconium oxychloride octahydrate (zirconium salt).

1) Natural zeolite was rinsed for 2-3times, impurities were removed, and then dried in an oven at 105°C;

2) Weigh natural zeolite (mass g), anhydrous aluminum trichloride (mass g), zirconium oxychloride octahydrate (mass g), distilled water (volume ml) in the proportion of 10:3:1:50, solid-liquid ratio of about 3.6:1, adjust the pH to 7 with 1mol/L NaOH solution, and shake for 24h at 20°C in constant temperature water bath shaker at 150r/min;

3) After the reaction, the solid-liquid separation was carried out, and the zeolite was dried in an oven at 105°C;
4) The dried zeolite was put into muffle furnace and calcined at 400°C for 2 hours. After cooling, aluminum zirconium modified zeolite was obtained.

2) Experimental study on covering and releasing of modified zeolite

Take three transparent plastic cylinders numbered 1-3 respectively, and mix the pretreated sediment evenly and lay it in the cylinder. Set the laying thickness as 3cm, the laying particle size as 0.5-1mm aluminum zirconium modified zeolite, and the laying thickness as 0.25, 0.5 and 1cm. After laying, use syringe to slowly inject 1.2L of self supplied water along the side wall of the cylinder, so as to avoid the disturbance of water flow to the sediment as much as possible. Close the bottle mouth to avoid pollution and put it in a cool place away from light. The test period is 30 days, and the sampling days are set as 1, 2, 3, 5, 7, 10, 15, 20, 25 and 30 days. Each time, use syringes to collect 100ml water samples from the place 30cm below the water surface of two cylinders respectively, put them into plastic bottles for numbering, put them into refrigerators for storage, and add the same amount of laboratory tap water to the cylinders after the completion of each regular collection of water samples. In the process of the test, the two indexes of ammonia nitrogen and phosphate in the water sample of the overlying water were detected and analyzed, and the detection method was based on the relevant national standards.

3. results and analysis

3.1. Effect of AZMZ covering on the releasing of nitrogen from sediment

Under static conditions, the control effect of using 0.5 ~ 1mm aluminum-zirconium modified zeolite with different coverage thickness on nitrogen release in sediment is shown in Figure 1. It can be seen from the figure:

(1) For figure (a), there is a certain difference in ammonia nitrogen concentration of overlying water under different covering thickness. For the coverage of 0.25cm, the concentration of ammonia nitrogen in the overlying water increased with the increase of test days, and for the coverage of 0.5cm and 1cm, the concentration of ammonia nitrogen in the overlying water hardly changed with the increase of test days.

(2) The test data in figure (a) is calculated by equation (12) to obtain figure (c). For figure (c), the thicker the overburden is, the more nitrogen release in the sediment is reduced, indicating the better the control effect. The reduction rates of 0.25cm, 0.5cm and 1cm were 57.6%, 78.8% and 89.1% respectively. Under different cover thickness, the control effect of nitrogen release in sediment is different. For the coverage of 0.25cm, the amount of nitrogen released from the sediment decreased with the increase of the test days in three stages, first increasing gradually, then almost unchanged, and finally decreasing, indicating that the coverage of 0.25cm had a certain control effect on the release of nitrogen in the sediment in the first and middle stage of the test, and the later control effect was weakened, and the release of nitrogen in the sediment could not be effectively controlled; for the coverage of 0.5cm and 1cm For example, the reduction of nitrogen release in sediment increased with the increase of test days, which indicated that 0.5cm and 1cm mulching could continuously control the release of nitrogen in sediment. However, covering 0.5cm can effectively control the release of nitrogen in the sediment, and covering 1cm has better control effect, which shows that the release of nitrogen reduction can be maintained at a higher level. In addition, according to formula (13), the saturated adsorption capacity of ammonia nitrogen of 0.25, 0.5 and 1cm aluminum-zirconium modified zeolite is 199.47, 398.94 and 797.87mg, respectively. Assuming that the reduction of nitrogen release in sediment is caused by the adsorption of aluminum-zirconium modified zeolite, the data shown in the figure are accumulated to calculate the nitrogen released from 0.25, 0.5 and 1cm aluminum zirconium modified zeolites The adsorption capacity of 0.25cm, 0.5cm and 1cm AZMZ is far less than the saturated adsorption capacity. However, covering 0.25cm can not effectively control the release of nitrogen in the sediment, which may be due to the small physical barrier effect, and can not effectively block the diffusion of ammonia nitrogen in the interstitial water between the AZMZ Attached.
(3) The test data in figure (a) is calculated by equation (10) to obtain figure (c). For figure (c), the thicker the overburden, the slower the average release rate of nitrogen in the sediment, indicating the better the control effect. Under the condition of 30 days study, the average release rate of nitrogen in the sediment without mulching is 17.48mg/(m²·d). According to the calculation of equation (14), under this condition, the effective duration of 0.5cm and 1cm mulching for nitrogen release control in the sediment is 8 years and 16 years respectively, which can control the release of nitrogen in the sediment for a long time, and the period is far longer than the period of experimental study.

(A) Ammonia nitrogen concentration releasing from contaminated sediment covered with different size of AZMZ

(B) Reduction of ammonia nitrogen releasing from contaminated sediment
3.2. Effect of AZMZ covering on the releasing of phosphorus from sediment

Under static conditions, the control effect of using 0.5-1mm AZMZ with different coverage thickness on phosphorus release in sediment is shown in Figure 2. It can be seen from the figure:

(1) For figure (a), there is a certain difference in phosphate concentration of overlying water under different covering thickness. For the coverage of 0.25cm, the phosphate concentration of the overlying water increases with the increase of the test days, and for the coverage of 0.5cm and 1cm, the phosphate concentration of the overlying water hardly changes with the increase of the test days.

(2) The test data in figure (a) is calculated by equation (12) to obtain figure (c). For figure (c), the thicker the overburden is, the more phosphorus is released from the sediment, indicating the better the control effect. The reduction rates of phosphorus release in sediment were 50.3%, 66.3% and 75.3% by covering 0.25, 0.5 and 1cm respectively. Under different cover thickness, the control effect of phosphorus release in sediment is different. For the coverage of 0.25cm, the release amount of phosphorus in the sediment decreased with the increase of test days in three stages, first increasing gradually, then almost unchanged, and finally decreasing, indicating that the coverage of 0.25cm had a certain control effect on the release of phosphorus in the sediment in the first and middle period of the test, and the later control effect was weakened, which could not effectively control the release of phosphorus in the sediment; for the coverage of 0.5cm and 1cm For example, the amount of phosphorus released from the sediment decreased with the increase of test days, indicating that 0.5cm and 1cm coverage could control the release of phosphorus in the sediment continuously. However, covering 0.5cm can effectively control the release of phosphorus in the sediment, and covering 1cm has better control effect, which shows that the release of phosphorus reduction is maintained at a higher level. In addition, according to formula (13), the saturated phosphate adsorption capacity of 0.25, 0.5 and 1cm AZMZ coating is 73.61, 147.22 and 294.44mg, respectively. Assuming that the reduction of nitrogen release in sediment is due to the adsorption of AZMZ coating, the data shown in the figure are accumulated to calculate the phosphorus released by 0.25, 0.5 and 1cm AZMZ coating on sediment The adsorption capacity is 2.67, 3.52 and 4.00mg, respectively. It can be seen that the adsorption capacity of 0.25, 0.5 and 1cm AZMZ is far less than the saturated adsorption capacity, and the failure of 0.25cm AZMZ to effectively control the release of phosphorus in the sediment may be due to its small physical barrier effect, which can not effectively block the diffusion of phosphate in the interstitial water between the AZMZ to carry out continuous and effective adsorption.

(3) Calculate the test data in figure (a) to get figure (c). For figure (c), the thicker the overburden,
the slower the average release rate of phosphorus in the sediment, indicating the better the control effect. Under the condition of 30 days study, the average release rate of phosphorus in the sediment without mulching was 3.61 mg/(m²d). Under this condition, the effective duration of 0.5 cm and 1 cm mulching on the control of phosphorus release in the sediment was 14 years and 28 years respectively, which could control the release of phosphorus in the sediment for a long time, and the period was far longer than the period of experimental study.

(A) Change of phosphate concentration with time in overlying water

(B) The change of phosphorus release from overlying water with time
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4. conclusion
In this study, the sediment of Maozhou River in Shenzhen was used as the test material, and AZMZ was used as the covering material. The static release simulation test was used to study the release of nitrogen and phosphorus through the covering layer. The main conclusions are as follows:

(1) Under the static condition, the aluminum zirconium modified zeolite with the particle size of 0.5-1mm is used to cover the sediment. The thicker the covering layer is, the slower the average release rate of nitrogen and phosphorus in the sediment is. The more the release amount of nitrogen and phosphorus in the sediment is reduced, the better the control effect is. Under the research conditions, the release of nitrogen and phosphorus in the sediment can be effectively controlled when the thickness of AZMZ coating is 0.5cm. The reduction rate of nitrogen and phosphorus release in sediment by 1cm AZMZ coating is 89.1% and 75.3% respectively, and the effective control time of nitrogen and phosphorus release in sediment is 16 years and 28 years respectively.

(2) Under static condition, the thicker the AZMZ cover, the smaller the contribution of the adsorption of the cover to the control effect of nitrogen and phosphorus release in the sediment, and the greater the contribution of physical barrier. Under the condition of proper physical barrier, the stronger the adsorption, the longer the effective duration of nitrogen and phosphorus release control.

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