The effect of capping with natural and modified zeolites on the release of phosphorus and organic contaminants from river sediment

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Abstract A microcosm system that included river sediment, water and different zeolite capping materials (natural zeolite, surfactant-modified zeolite (SMZ), or aluminum modified zeolite (AMZ)) was designed to study the effect of capping on the release of phosphorus and three organic pollutants (phenol, pyridine, and pyrene) from the sediment to the overlying water over the course of three month. For the same amount of the three capping materials, the efficiency of phosphorus inactivation was in the order of SMZ > AMZ > natural zeolite. The inactivation of phosphorus was mainly caused by the covering effect, co-precipitation and adsorption by the capping materials. The different zeolites gave different results for the release of phenol, pyridine, and pyrene from the sediment. When natural zeolite was used as the capping material, there was no effect on the release of pyrene and pyridine, whereas capping the sediment with SMZ or AMZ inhibited the release of pyrene and pyridine but to different extents. However, for controlling the release of phenol from the sediment, aluminum modified zeolite was the most efficient material, whereas no effects were observed when natural zeolite or SMZ were used. The different capabilities of the zeolite materials for controlling the release of different organic pollutants are related to the differences in the electrical properties of these pollutants.

Keywords sediment, capping, natural zeolite, modified zeolite, phosphorus

1 Introduction

Sediments are a sink as well as a source for nutrients and

therefore play a decisive role in eutrophication. An abundance of phosphorus(P) which in most systems is the growth-limiting nutrient, initiates phytoplankton blooms as well as the development of cyanobacteria, which can severely deteriorate water quality. In spite of reductions in external P-loading in many eutrophic lakes, high P concentrations are still often observed in these lakes during the summer. This phenomenon is generally caused by P-release from a large mobile P-pool in the sediment. This internal loading may keep the body of water in a eutrophic state for years even after the reduction of the external loadings [1]. Many different restoration methods have been used in order to reduce internal P loading such as: hypolimnetic aeration [2], sediment removal [3], calcium addition [4], Fe^{3+} addition [5] and Al^{3+} addition [6,7]. Jacobs and Forstner [8] developed the concept of subaqueous capping of contaminated sediments with active barrier systems (ABS) in order to minimize the contaminant release into the surface water. This means that in situ capping of the sediment surface with a layer containing a reactive component that immobilizes P, may be applied.

In this study, the reactive material chosen was natural and modified zeolites which have previously been used to remove heavy metal cations in water columns [9,10], and have been used for P-fixation in laboratory tests [11,12]. Use of zeolites as a reactive compound has a number of advantages. It is a readily available non-toxic material and exhibits physical and chemical stability over the long-term [13,14]. Moreover, it can actively block contaminants. Natural zeolites are capable of demobilizing large amounts of cationic pollutants by sorption and they can demobilize non-polar organics and anionic contaminants when the zeolite surface is pretreated with cationic surfactants [9–12]. But little emphasis has focused on how inorganic salt modification affects the efficiency of zeolites.

In this work, the investigations mainly focused on the

processes of P fixation by natural and modified zeolites in an aquatic environment. For this purpose, P fixation capacities of several zeolites were studied in agitation experiments using deionized water and different P concentrations. Additionally, long-term incubation experiments were carried out with Haihe River sediment using various zeolites as barriers. During the incubation process, three organic pollutants (phenol, pyridine, and pyrene) were added to the sediment to evaluate the capacity of the capping materials to simultaneously remove P and organic pollutants.

2   Materials and methods

2.1   Sediment

The sediment used in the experiments was collected in October 2005 from the Haihe River, China. The surface sediment (top 10 cm) was collected with a stainless steel scoop and then placed into polytetrafluoroethylene (PTFE) bags. All the samples were immediately transferred to the laboratory and kept at $-20°C$ in the refrigerator. The samples were freeze-dried, homogenized and passed through a 150 μm sieve. All the equipment used for sample collection, transportation, and preparation were free from phosphorus contamination. The sediment samples were analyzed for total nitrogen (TN) [15] and total P (TP) [16] (SMT protocol). Water content and loss on ignition measurements were based on weight loss after drying and combustion of the sediment at 105°C and 550°C, respectively. Total organic carbon (TOC) in the sediment was determined after treatment of the sample with $K_2Cr_2O_7/H_2SO_4$ according to the Walkey-Black Method [17]. Table 1 shows the main properties of the sediment used in the experiments.

2.2   Barrier materials

Three different materials including natural zeolite, surfactant modified zeolite and aluminum modified zeolite were used as the barrier materials for the experiments with the river sediment. Table 2 shows the main chemical composition of the natural zeolite with a grain size of 0.15–0.30 mm.

The preparation of SMZ: hexadecyltrimethylammonium bromide (HDTMA-Br) was used for the surface modification. An HDTMA aqueous solution with initial concentra-

tion of 200 mmol/kg was mixed with natural zeolite to produce SMZ. The HDTMA-zeolite mixture was shaken on a shaker table at 160 rpm for 24 h at 25°C followed by centrifugation and washing several times with deionized water. The surfactant-modified samples were then air-dried prior to further use [18,19].

The preparation of aluminum modified zeolite: aluminum chloride was used for surface modification. Natural zeolite and aluminum chloride were mixed with a mass ratio of 4:1. The mixture was then placed in deionized water and shaken on a shaker table at 160 rpm for 24 h at 25°C followed by centrifugation and washing several times with deionized water. The aluminum-modified samples were then air-dried prior to further use [20].

2.3   Experiment design

2.3.1   Phosphate adsorption experiments

Batch experiments were carried out to investigate the adsorption of phosphate onto the natural and modified zeolite materials. Solutions of KH_2PO_4 were prepared with initial phosphorus concentrations of 1.0–50 mg/L. Aliquots of 50 mL were added to 0.5 g of zeoltie in 100-mL centrifuge tubes. The samples and appropriate blanks were shaken mechanically at 25°C for over 24 h to reach equilibrium. The samples were then centrifuged and filtered through a 0.45 μm GF/C filter membrane. The filtrate was analyzed for soluble reactive P (SRP) using the molybdenum blue/stannous chloride method [21]. Triplicate analyses were performed on all samples and the final data are expressed as the average value.

2.3.2   Incubation experiments

The experiments to study the release of P from the nutrient-rich sediments covered by different zeolites barriers were carried out in the dark at 25°C in anoxic media.

To simultaneously determine the release of organic pollutants from the sediments with different caps, the sediments were spiked with three methanol solutions containing 200 mg/L of phenol, pyridine, or pyrene and then placed in a fume hood for four hours to volatilize the solvents. Before use, the contaminated sediments were sealed and placed in darkness for two days to age the pollutants. The pre-analysis of the sediment indicated that

Table 1   Chemical properties of the sediment

pH	Water content /%	TOC /%	TN /(mg·kg^{-1})	TP /(mg·kg^{-1})
7.89	86.3	6.37	5230	1960

Table 2   Chemical composition of natural zeolite

Composition	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	K$_2$O	CaO	MgO	Na$_2$O
Content/%	65.90	13.24	0.87	2.09	2.86	0.62	2.59

the background level of these pollutants was negligible. Therefore, the final spiked concentration of each of these three pollutants in the sediment was about 1.0 mg/kg.

A set of experiments was carried out with sediments cores of 200 g (5 cm length) and 1 L of deionized water as the overlying water. One core was used as the reference and was kept without a barrier. The others were capped by a 2 cm thick layer of natural or modified zeolite. The incubation experiments lasted for 90 days. Samples of the overlying water (5 mL) were removed every few days, with a syringe and analyzed. A new aliquot of deionized water was then added to maintain a constant water volume.

2.3.3   Analysis methods

The SRP analyses of the water samples were performed by the molybdenum blue/stannous chloride method [21]. A Waters 1525 high-performance liquid chromatograph (HPLC), with a Waters C18 column (μ Bondapak 3.9 mm i.d.×300 mm×10 μm, Waters Corp., USA) was used for analysis of the organic pollutants. The mobile phase was acetonitrile:water (80:20, v/v), and the flow rate was 1.0 mL/min. A Waters 2475 fluorescence (FL) detector (Waters Company, USA) was used in the analyses and the excitation and emission wavelengths were optimized for detection of the three target organic pollutants: 280/355 nm (for pyrene), 254/390 nm (for pyridine), and 233/302 nm (for phenol). All measurements were done in duplicate and the uncertainty was generally less than ±5%. The average data are used for discussion.

3   Results and discussion

3.1   Effects of zeolite barriers on the phosphorus release from sediments

The incubation experiments showed that without a barrier, the SRP concentration in the overlying water increased to 2.78 mg/L within 90 days (Fig. 1), which corresponds to an SRP flux of 3.54 mg/(m^2·d), A natural zeolite barrier with a thickness of 2 cm led to a decrease in the SRP flux of about 53.6%, and a maximum SRP concentration of 1.29 mg/L was achieved. The increase in SRP concentration corresponds to an SRP flux of 1.64 mg/(m^2·d). SMZ and aluminum modified zeolite barriers with a thickness of 2 cm led to a decrease in the SRP flux of 77.3% and 67.3%, respectively. The maximum SRP concentrations were 0.63 and 0.91 mg/L and the corresponding SRP fluxes were 1.16 and 0.80 mg/(m^2·d), respectively.

3.2   Adsorption isotherms of phosphate on natural and modified zeolite

The following three models can be used to describe the adsorption isotherms of phosphate on the zeolites.
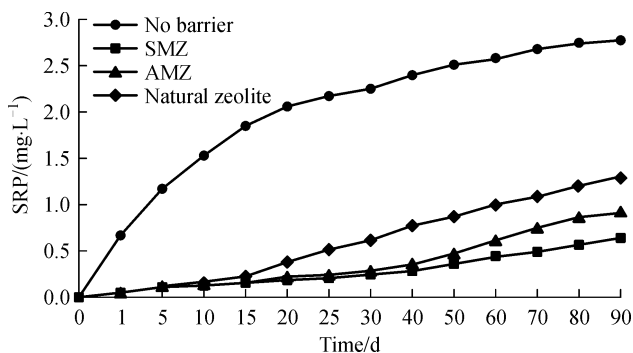
Fig. 1   Influence of different zeolite barriers on the P release from the sediment (25°C, pH 7.0)

$$\text{Linear model}: Q = KC + b, \tag{1}$$

$$\text{Freundlich model}: Q = KC^n, \tag{2}$$

$$\text{Langmuir model}: Q = \frac{Q_{max}\,KC}{1 + KC}, \tag{3}$$

where Q is the phosphate adsorption rate, Q_{max} is the maximum phosphate adsorption rate, C is the adsorption equilibrium concentration, K is the adsorption coefficient, and b and n are constants.

The sorption of phosphate from an aqueous solution onto the natural and modified zeolite materials is shown in Fig. 2. The results indicate that the adsorption rate increases initially as the equilibrium concentration increases and then reaches saturation. The leveling of the isotherm is probably due to fewer active sites being available to phosphate when C is larger and/or the difficulty of the edge molecules in penetrating the adsorbent since the phosphate molecules partially cover the surface sites. The results of the three absorbents best fit with a Freundlich equation. The corresponding parameters are shown in Table 3.

According to Fig. 2 and Table 3, it can be concluded that surface modification of natural zeolite increases the phosphate adsorption capacity. The order of the phosphate adsorption capacity is SMZ > AMZ > natural zeolite.

The potential sorption mechanism of SMZ includes sorption due to admicelle formation, chemical reduction of anions to less soluble forms and/or surface precipitation of oxyanions with HDTMA [18,19,22]. For the AMZ, the substitution of silicon with aluminum may cause the changes in the capacity and thus increases the anion sorption capacity [20].

Table 3   Parameters of Freundlich isotherm sorption Equaption (25°C)

	K	N	R^2
Natural zeolite	9.56	0.96	0.99
SMZ	230.48	0.63	0.95
AMZ	88.56	0.75	0.96
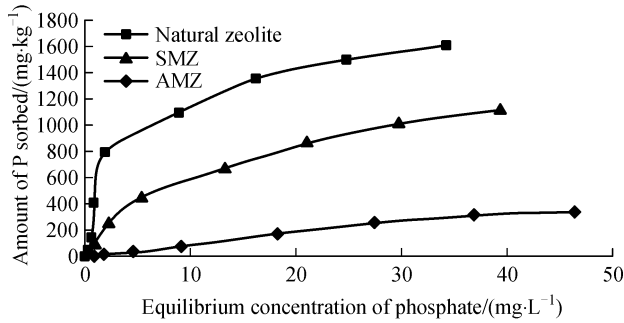
Fig. 2 Sorption isotherms of phosphate on zeolite materials (25°C, pH 7.0)

3.3 Mechanisms of phosphorous fixation

Due to the net negative charge on the framework, natural zeolites have little or no affinity for anions. It has been reported by Komarowski et al. [23] that natural zeolite is not very effective for reducing phosphate from secondary treated municipal wastewater using a batch process. Likewise, Widiastuti et al. reported that less than 15% of phosphate was removed using Australian natural zeolite [24]. So the sorption effect of natural zeolite on P fixation in sediments can be neglected.

In the present incubation experiments, about 50% of the phosphate was removed using natural zeolite (Fig. 1). Wild et al. [12] concluded that when NH_4^+ and PO_4^{3-} were simultaneously removed from an aqueous solution using zeolites, NH_4^+ was removed by a cation exchange reaction with the zeolite, whereas the Ca^{2+} in zeolite contributed to the removal of PO_4^{3-} due to the formation of the precipitate $Ca_3(PO_4)_2$. The sediments in experiment also released NH_4^+ during the P release process, so it can be assumed that the NH_4^+ exchanged with the Ca^{2+} which then contributed to the P fixation by co-precipitation.

From Fig. 1, it can also be concluded that the capacity of P removal of the three capping materials is SMZ > AMZ > natural zeolite, which is in accordance with the results of the adsorption batch experiments. This result might imply that the adsorption capacity is the most important factor that affects the capacity of the capping material to fix the P in the sediments.

However, in addition to the co-precipitation of the P with calcium and the adsorption of P by the capping materials, the capping materials also isolate the sediments from the overlying water, which can also contribute to the P fixation.

3.4 Effect of capping on the release of polar and non-polar organic contaminants

Capping is also a useful method to deal with sediments polluted by different organic contaminants. The release of different types of organic contaminants (phenol, pyridine,

and pyrene) was tested at the same time as the P fixation tests were conducted. The pyrdine (1 mg/kg) in the incubation system was gradually released to the overlying water over the course of 12 days and then reached equilibrium with a concentration of 190 µg/L (Fig. 3). The natural zeolite had little effect on the release of pyrdine from the sediments. However, the modified zeolites, especially the SMZ, effectively inhibited the release of the pyrdine to < 90 µg/L after 30 days.

Since the surface of soil and sediments are usually negatively charged, phenol, as a weak anionic organic pollutant, only weakly adsorps to the sediment particles [25]. Therefore, it was released to the overlying water more quickly and reached a maximum concentration in four days (Fig. 4). Its concentration then decreased quickly through partitioning to the sediments, volatilization, and oxidation. The concentration of phenol in the overlying water capped with AMZ was less than 10 µg/L during the whole incubation process, which implies that this kind of modification could effectively inhibit the release of anionics from sediments [26].

The concentration of pyrene, a nonpolar organic pollutant, in the overlying water also reached a maximum concentration in four days (Fig. 5). The natural zeolite had little effect on the release of the pollutant and SMZ had the largest effect. The concentration of the pollutant capped
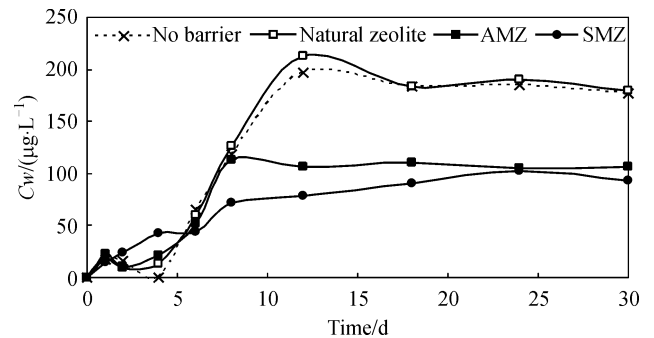
Fig. 3 Influence of different capping materials on pyridine release (25°C, pH 7.0)
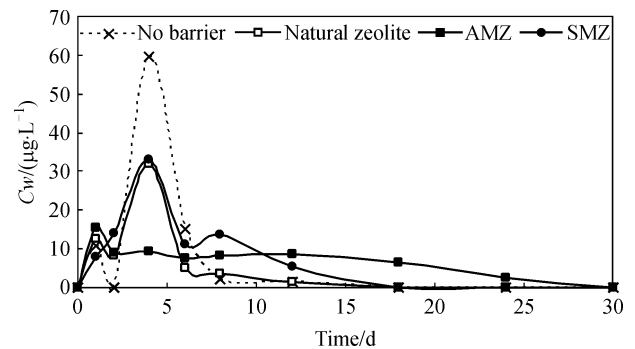
Fig. 4 Influence of different capping materials on phenol release (25°C, pH 7.0)
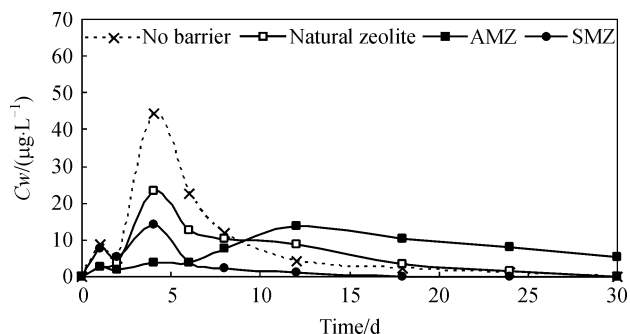
Fig. 5 Influence of different capping materials on pyrene release (25°C, pH 7.0)

with SMZ reached a maximum of 14 µg/L on the fourth day and then it decreased quickly to less than 5 µg/L. This is probably due to the enhancement of adsorption affinity between the zeolite material and the pyrene [19,27]. AMZ also inhibited the release of the pyrene, with a maximum concentration of 13.6 µg/L on the 12th day.

4 Conclusions

Surface modification increased the phosphate adsorption capacity of natural zeolite. A Frundlich adsorption isotherm was the best fit for the experimental data for all three zeolite materials which included natural zeolite, surfactant-modified zeolite (SMZ) and aluminum modified zeolites (AMZ). The adsorption capacity for the three materials was in the order of SMZ > aluminum modified zeolites > natural zeolites. A zeolite barrier of 2 cm effectively prevented P release from the sediments. With the same amount of the three capping materials applied, the efficiency of P inactivation was in the order of SMZ > aluminum modified zeolites > natural zeolites, which is consistent with the adsorption capacity of the three materials.

The inactivation of phosphorus was mainly caused by the covering effect, co-precipitation and adsorption of the capping materials. Aluminum modified zeolite had a significant effect on inhibiting the release of anionic organic pollutants from the sediments, whereas surfactant-modified zeolite was the most effective for controlling the release of pyrene. The modification of zeolite as a capping material was not as effective for controlling the release of cationic organic pollutants such as pyridine.

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