



# Application of zeolite/hydrous zirconia composite as a novel sediment capping material to immobilize phosphorus



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## ARTICLE INFO

### Article history:

Received 10 January 2017

Received in revised form

15 April 2017

Accepted 11 June 2017

Available online 12 June 2017

### Keywords:

Adsorption

Capping

Phosphorus

Sediment

Zeolite

Zirconia

## ABSTRACT

A unique sediment-capping agent consisting of a zeolite/hydrous zirconia composite (ZHZ) was developed and tested for P-immobilization in the overlying water and sediment cores from a freshwater pond. In the ZHZ, NaP1 zeolite was covered with hydrous zirconia, which existed as an amorphous phase. Experimental results in pond water indicated that ZHZ could efficiently remove soluble reactive phosphorus. The 28-day sediment incubation experiments showed that capping sediment with ZHZ resulted in a more efficient, rapid and sustained decrease in P concentration when compared with the traditional alum treatment method. Furthermore, ZHZ increased the sediment stability, resulting in the lowest turbidity, total phosphorus and soluble reactive phosphorus concentrations in overlying water following artificially induced resuspension of sediment. Phosphorus fractionation of sediment showed that the dominant P form transferred from HCl-extractable P to residual P, and the most release-sensitive P (labile P and reductant reactive P) was decreased after ZHZ application. Overall, ZHZ is a highly effective P-immobilization material. ZHZ has high potential as a sediment capping material to control internal P loading in eutrophic water bodies.

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## 1. Introduction

Ponds are important water resources that provide values such as recreation, fish breeding, and habitat for wetland plants and animals (and are, therefore, an important source of biological diversity in the landscape). Globally, though the covered total surface area is much lower, small water bodies greatly outnumber large ones (Downing et al., 2006; Verpoorter et al., 2014). A recent study using high-resolution satellite imagery showed that though there are about 117 million lakes greater than 0.002 km<sup>2</sup>, covering a total area of 5.0 × 10<sup>6</sup> km<sup>2</sup>, there are only 27 million water bodies larger than 0.01 km<sup>2</sup> with a total surface area of 4.76 × 10<sup>6</sup> km<sup>2</sup> (Verpoorter et al., 2014). Phosphorus (P) is usually the limiting nutrient for the growth and proliferation of algae in relatively closed water bodies such as lakes, reservoirs and ponds (Cooke et al., 2005; Manuel, 2002). Worldwide, enrichment of P in these water bodies causes serious deterioration of water quality. Measures for the reduction of P in the water bodies are thus required to restore the ecological structure and function of the aquatic

ecosystems. To this end, reduction measures for both internal P loading and external catchment P loading are important.

Regarding the internal P loading, an in situ geo-engineering method using sediment capping agents is one of the most investigated and practically used reduction measures (Cooke et al., 2005; Hickey and Gibbs, 2009; Spears et al., 2013; Zamparas and Zacharias, 2014). Though Fe-, Al- or Ca-based soluble metal salts (especially alum) have been intensively investigated and also put into use for restoration in many lakes worldwide, these materials may significantly change the pH of lake water and lead to negative effects on aquatic organisms (Hupfer and Hilt, 2008; Gensemer and Playle, 1999; Reitzel et al., 2013; Stumm and Morgan, 1996). Furthermore, the reductive condition that exists in eutrophic lakes can result in the liberation of P that is bound to Fe (Hupfer and Hilt, 2008; Gensemer and Playle, 1999; Reitzel et al., 2013; Stumm and Morgan, 1996). In recent years, use of insoluble solid adsorbents has attracted growing interest. Similarly to the metal salts, addition of solid adsorbents can remove P from the water column and reduce the release of P from sediment once settled onto the surface of the sediment bed. A number of adsorbent materials have been investigated recently as sediment capping agents; these include Al-modified zeolite (Gibbs and Özkundakci, 2011; Özkundakci et al., 2010), calcite (Berg et al., 2004; Lin et al., 2011; Prepas et al.,

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2001), chitosan-modified local soils (Pan et al., 2012), and particularly the La-modified bentonite clay, Phoslock (Akhurst et al., 2004; Bishop et al., 2014; Copetti et al., 2016; Egemose et al., 2010; Gibbs et al., 2011; Lürling and Faassen, 2012; Lürling et al., 2016; Meis et al., 2012, 2013; Robb et al., 2003; Spears et al., 2016; Waajen et al., 2016).

Owing to the high affinity of zirconium for phosphate, zirconium (hydr)oxide and zirconium-loaded materials have been widely investigated for phosphate removal from water (Chitrakar et al., 2006; Liu et al., 2008; Peterson et al., 1974; Rodrigues et al., 2012; Su et al., 2013; Wang et al., 2016). Zirconium is widely distributed in nature and its concentration within the earth's crust is approximately 130 mg/kg (Nielsen, 2005), making it the 19th most abundant of all elements and more abundant than zinc and copper. Zirconium is also found in all biological systems. The human body contains, on average, 250 mg of zirconium, and daily intake is approximately 4.15 mg (3.5 mg from food and 0.65 mg from water), depending on dietary habits (Schroeder and Balassa, 1966). Zirconium compounds are of generally low toxicity, and zirconia is even safer when compared with other zirconium compounds (U.S. Department of Health and Human Services, 1978). Owing to the strong phosphate adsorption and low solubility of formed Zr-phosphate complexes (Chitrakar et al., 2006; Liu et al., 2008; Peterson et al., 1974; Rodrigues et al., 2012; Su et al., 2013; Wang et al., 2016), zirconium-containing materials may be good alternatives to existing materials as P-inactivation agents in lakes and ponds.

The worldwide use of coal in electricity/heat generation processes produces great amounts of coal fly ash every year as a by-product. It was estimated that 349 Mt of fly ash was produced worldwide in 2000 (Wang and Wu, 2006) and was over 750 Mt in 2012 (Blissett and Rowson, 2012). Internationally, only a part of coal fly ash is reused. For instance, the reutilization rate is 39% for the United States (Blissett and Rowson, 2012), 47% for Europe (Blissett and Rowson, 2012), and 68% for China (Tan et al., 2014). As a result, a huge amount of coal fly ash is impounded or land filled which not only occupies a lot of land, but also causes serious environmental pollution problems. We have been interested in the recycling and value-added reuse of coal fly ash through synthesis of zeolite-based products. Zeolite preparation from coal fly ash using traditional synthesis process produces not only zeolite product but also leaves behind large amounts of problematic waste alkaline solution. We have recently initiated a novel method to synthesize zeolite/hydrous metal oxide hybrid material by introducing a reaction step into the traditional zeolite synthesis route that involves neutralizing waste alkaline solution with soluble metal salts (Xie et al., 2013, 2014). The composites were shown to have high capacity to simultaneously retain phosphate (anionic species) and ammonium (cationic species) (Xie et al., 2013, 2014). Since hydrous zirconia has good affinity toward phosphate and zirconium is affordable, non-toxic and environmentally friendly (Nielsen, 2005; Schroeder and Balassa, 1966), we consider that use of soluble zirconium salts in our one-pot synthesis process could develop a zeolite/hydrous zirconia composite (ZHZ) for retention of nutrients. Because the raw material is coal fly ash which is a solid waste generated in large amounts worldwide, synthesis of large amount of ZHZ with cost-effectiveness is possible for large scale use in the nutrients reduction in water bodies. Though many compounds are being synthesized previously, many of the strong P sorbents in the literature are simply far too expensive to be applied on a large scale in lakes and ponds (Lürling et al., 2016). The aims of the current study were (i) to prepare ZHZ and examine its performance for phosphorus immobilization in batch experiments; (ii) to assess the ability of ZHZ as a pond sediment capping agent to reduce the concentrations of P during a 28-day incubation period; and (iii) to compare the

performance of ZHZ with that of alum as a sediment capping agent.

## 2. Materials and methods

### 2.1. Study site

The pond for our study is situated at 31° 1.35' N, 121° 25.5' E in the botanical garden of the Minhang campus of Shanghai Jiao Tong University. This shallow water body has an approximate surface area of 0.5 ha with an average depth of ~1.45 m (ranging from 1 m to 2.7 m). The pond mainly serves as an important recreational area in the campus, but many ducks as well as several kinds of fish (mainly silver carp and grass carp) inhabit the pond. The pond has neither a natural surface water inlet nor outlet. Water leaves the pond by evaporation while the input of water is from rainfall and intermittent pumping from a nearby river. Before this study, we measured the nutrient status of the pond for one year (twice each month) and found that the concentrations of various water quality parameters were: total nitrogen 0.54–2.94 mg/L (average 1.18 mg/L), total phosphorus 0.08–0.71 mg/L (average 0.23 mg/L), ammoniacal nitrogen 0.027–0.095 mg/L (average 0.058 mg/L), COD<sub>Cr</sub> 13.86–30.79 mg/L (average 21.49 mg/L), and turbidity 17.7–43.8 FAU (average 31.16 FAU).

### 2.2. Materials

The ZHZ product was obtained according to the procedure (with minor modifications) described in our previous studies for the preparation of zeolite/hydrous aluminum (or iron) oxides (Xie et al., 2013, 2014). Briefly, zeolite was synthesized by first mixing 150 g of coal fly ash with 900 mL of 2 M NaOH solution and allowing the mixture to react at 95 °C for 24 h to generate zeolite and waste alkaline solution. After the mixture cooled to room temperature, 900 mL of 0.5 M ZrOCl<sub>2</sub> solution was added into the suspension dropwise (10 mL/min) as it was stirred. The stirring continued for another 4 h after the addition process. The solid ZHZ phase was finally separated, washed, dried, and ground in a manner similar to that previously reported (Xie et al., 2013, 2014).

Clear acrylic tubes with an inner diameter of 7 cm and a length of 70 cm were utilized as both sediment samplers and incubation vessels. Before sediment sampling, the tube was placed vertically onto the pond bed. Both the water depth line and the 20 cm line above the water depth line were marked on the sampler and then the tube was inserted into sediment until the 20 cm line reached the water surface. Intact sediment cores 20 cm in length and 7 cm in diameter were extracted from the pond on July 18, 2015. Once a core was extracted, the bottom of the incubation tube was immediately sealed with a screw cap, and the cores were placed vertically in a plastic lattice frame. A sample (80 L) of the corresponding overlying water was also collected at the site. The cores and water sample were transported back to an incubation chamber of our laboratory immediately after the collection and the 28-day incubation experiments, as well as subsequent agitation experiments, were conducted. Chemical analyses of the initial (pre-study) water samples collected are shown in Table 1 and those for sediment are given in Table 2.

### 2.3. Characterization of materials

The chemical composition of zeolite, ZHZ and sediment was determined by X-ray fluorescence analysis (PW2404, Philips Company). The mineralogical composition was identified by powder X-ray diffraction (XRD) analysis (D/max 2550VL/PC) with Cu-K $\alpha$  filtered radiation (30 kV, 15 mA). Scanning electron microscopy (SEM) images were obtained using a Tabletop Microscope (Hitachi

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