Application of synthetic iron-oxide coated zeolite for the pollution control of river sediments

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HIGHLIGHTS

- The coated iron oxides enhance the phosphate and sulfide removal by zeolite.
- IOCZ owns great capacities to sorb ammonia, phosphates and sulfides in solution.
- The phosphates favor the ammonia retardation by IOCZ.
- Most retarded pollutants on IOCZ are stable enough not to release.
- Redox between Fe(III) and S(II) was the main mechanism for sulfide sorption.

GRAPHICAL ABSTRACT
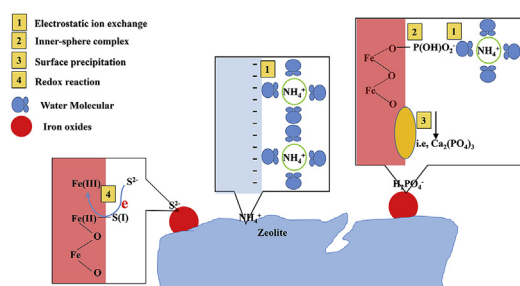
ABSTRACT

Contaminants released from river sediments are catching more attentions for river environmental management, especially when external sources of river pollution have been well controlled. To reduce the contaminant release from sediments, in-situ capping is often applied because of its effective reduction of contaminant flux and minimal disturbance to the surroundings. As an innovative sediment capping material, iron-oxide coated zeolite (IOCZ) was synthesized, characterized, and evaluated in this study. Its performance for the NH_4^+-N, PO_4^{3-}-P, and S^{2-}-S fixation in aqueous solutions was evaluated using batch and fixed-bed column experiments. IOCZ was found effective as a sorbent for NH_4^+-N, PO_4^{3-}-P, and S^{2-}-S with the maximum Langmuir sorption capacities of 6.23 mg N g^{-1}, 0.966 mg P g^{-1}, and 1.70 mg S g^{-1}, respectively. Under the studied conditions, the whole breakthrough process in the fixed-bed column could be well described by Thomas model, indicating IOCZ can effectively retard NH_4^+-N, PO_4^{3-}-P, and S^{2-}-S under flowing conditions. In addition, desorption simulative experiments suggested that the retarded pollutants were stable even under some extreme environments such as flooding or tiding. Therefore, IOCZ seems a promising capping material to control the release of NH_4^+-N, $H_2PO_4^-$-P, and S^{2-}-S from river sediments.

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1. Introduction

Some problems of river water quality in South China come from

polluted sediments, which is an important sink of many critical contaminants, such as ammonia, phosphorus, sulfide and heavy metals (e.g. Pb, Cu and Hg). Ammonia and phosphorus stimulate excessive algae growth in water bodies. When algae decompose, they quickly deplete dissolved O_2, deteriorating the quality of life forms. High content of sulfides in sediments is often accompanied with black or brown color and rotten egg odor in water (Rickard and Morse, 2005). Eutrophication, sulfides, and heavy-metal bio-accumulation have posed a threat to public health, especially when hydraulic disturbances in sediments that have been deposited at river bottom cause these pollutants to be released back to the river water. Therefore, proper remediation techniques are needed to address such releases.

Capping is a cost-effective strategy to prevent re-suspension, transport, and dissolution of pollutants from sediments into water, exposure to aquatic organisms, and finally to humans (Yin et al., 2010; Han et al., 2016). Capping can decrease transport paths for dissolved and/or colloid-bound contaminants toward biodegradation zone, to physically isolate sediments from bioturbating organisms, and to prevent physical mixing by wave or current. Active capping greatly enhances contaminant isolation from the overlying water column and benthic zone through stimulated degradation and/or contaminant sequestration by active materials.

Various materials have been studied or used for capping, including activated carbon, clay mineral, quartz sand, and so on (Tomaszewski et al., 2007; Cho et al., 2009; Xu et al., 2012). Among them, zeolite was the most frequently employed for inorganic contaminants, because of its high sorption capacity for cationic NH_4^+-N and heavy metals from solution (Lin et al., 2011; Huang et al., 2012; Wang et al., 2014b). Due to its mineralogical structure, zeolite is reported as an active barrier to prevent pollutants releasing back to the aqueous phase (Kang et al., 2016). However, zeolite seems not effective to sequestrate anionic phosphates and chromates (Kang et al., 2016; Lin et al., 2011). Therefore, Ca-modified zeolite and Al-modified zeolites (Hermassi et al., 2016), and surfactant modified zeolites (Sun et al., 2011) were developed to remove anionic phosphates and organic pollutants. In these studies, nevertheless, its performance for sulfide removal was not addressed at all.

Iron oxides have widely reported to have a great potential to simultaneously sequestrate anionic sulfides and phosphates in water. The reaction between dissolved sulfides and iron oxides is well-documented, and occurs in various natural and anaerobic environments effectively to retard the sulfides (Poulton et al., 2002). In some previous studies (Poulton et al., 2002; Su and Zhao, 2013), iron (hydr)oxides was found to effectively remove dissolved hydrogen sulfide from seawater with a distinct color change, due to the oxidation of sulfide by Fe(III) and the subsequent precipitation of the resulting Fe(II) with the additional sulfide. In addition, many studies reported the high capacity of iron oxides on phosphate sequestration. Therefore, the combination of zeolite and iron oxides seems a promising active capping material to simultaneously sequestrate cationic ammonia and heavy metals, as well as anionic sulfides and phosphates in sediments. To our knowledge, whereas, no study has explored the performance of iron oxide coated zeolite (IOCZ) on removal of ammonia, sulfides, and phosphates so far, although Zhao et al. (2010) investigated the adsorption behavior of IOCZ for methylene blue and methyl orange, and Poulton et al. (2002) examined its capacity to fix sulfides. In addition, the distinct characteristics of these two components (zeolite and iron oxides) may affect the surface behavior of different target contaminants, but it has not been thoroughly tested. Therefore, we synthesized and characterized the IOCZ, and compared its adsorption capacity for ammonia, phosphates and sulfides with unmodified zeolites (UMZ), via a series of batch and fixed bed

column experiments herein, aiming to research the feasibility of IOCZ as an active capping material for polluted sediments.

2. Materials and methods

2.1. IOCZ preparation and characterization

The UMZ (2–4 mm) used in this study was bought from Damao Chemical Corp., Tianjin. The IOCZ was synthesized in two steps: iron oxide preparation, followed by coating iron oxides on the bought zeolite. First, 200 mL 1 g mL^{-1} $FeCl_3$ solution was added in 185 mL of 10 M NaOH solution by dripping slowly; the resulting precipitates were flushed with deionized water for 3 or 4 times, and then dried in an oven of 110 °C for 20–21 h; the dry iron oxide powder was sequentially remoistened with deionized water as mud with 45% moisture. Second, each 100 g of UMZ was mixed with 10 g of iron oxide mud (dry mass), and kept the mud being uniformly coated on the surface of UMZ; the resulting zeolites were then dried at 110 °C for 20 h, cooled down to room temperature and flushed with deionized water until no weakly-associated iron oxides were released.

The vacuum densities of UMZ and IOCZ were determined through indirect volume measurement based on Archimedes principle, and their specific surface area were analyzed by ASAP2010 micro-pore analyzers (Micromeritics Co. Ltd., Norcross, GA, USA) with N_2 at 77.35 K. The point of zero charge (pH_{pzc}) of UMZ and IOCZ were determined using the method described by Milonjic et al. (1975). Their surface morphology was examined using J4800 Scanning Electron Microscope (SEM, Philips, Japan) by applying an electron acceleration voltage of 20.0 kV. The elemental composition on their surface was examined by energy dispersive X-Ray spectroscopy (EDX). X-ray powder diffraction data were collected with an PW1830X-ray powder diffractometer (Philips, Japan) equipped with a X'Celerator detector. Operating conditions were: monochromatised Cu Kα radiation, 40 kV, 200 mA, 2θ-range from 10 to 80, step rate of $2\theta = 0.05°/s$. To identify the functional groups present on the surface of UMZ and IOCZ, infrared spectra was obtained using Fourier transform infrared (FT-IR) Spectrophotometer (Perkin Elmer Spectrum Version 10.03.05). To investigate the mechanisms of pollutant sequestration, the X-ray photoelectron spectroscopic (XPS) spectra before and after pollutant sequestration were obtained with an PHI 5600X-ray photoelectron spectroscopy (Physical Electronics Inc., Chanhassen, MN, USA), equipped with a monochromated AlKα X-ray source (1486.6 eV, 500 μm spot size, 15 kV, 150 W). All XPS spectra were calibrated to the binding energy of Cs photoelectrons at 284.8 eV, and then analyzed with XPS PEAK 4.1 software.

2.2. Batch experiments

To investigate the retardation capacity of the UMZ and IOCZ for main pollutants in river sediments, we performed series of batch experiments, where 1.00 g of UMZ or IOCZ was mixed with 100.00 mL solution containing various concentrations of ammonia, phosphate or sulfides, at 250 mL conical flask on a 60 r min^{-1} shaker at room temperature (23 ± 2 °C) for various periods of time. During the shaking, to avoid the potential oxidation of pollutants by O_2 in air, the flask was completely sealed with a plastic film. In addition, a control without UMZ and IOCZ was conducted with NH_4^+ or S^{2-} solution to quantify the loss of sulfide due to O_2 oxidation. These mixtures were filtrated with 0.45 μm membranes, and the filtrate was then analyzed to monitor concentration change of these pollutants before and after sorption. The kinetic data were fitted with Lagergren 2nd order equation (Equ. 1) and the sorption isotherm data were simulated with Langmuir and Freundlich