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Synergistic adsorption of phosphorus by iron in lanthanum modified bentonite (Phoslock®): New insight into sediment phosphorus immobilization

Shiming Ding [a, *], Qin Sun [b], Xiang Chen [b], Qing Liu [b], Dan Wang [c], Juan Lin [a, d], Chaosheng Zhang [e], Daniel C.W. Tsang [f]

[a] State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China
[b] Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes, Ministry of Education, College of Environment, Hohai University, Nanjing 210098, China
[c] Shanghai Waterway Engineering Design and Consulting Co., Ltd., Shanghai 200120, China
[d] University of Chinese Academy of Sciences, Beijing 100049, China
[e] International Network for Environment and Health, School of Geography and Archaeology, National University of Ireland, Galway, Ireland
[f] Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

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ABSTRACT

Iron redox cycle plays a primary role in controlling the mobility of P in sediments. It is crucial to better understand how lanthanum (La) modified bentonite (LMB, Phoslock®), an increasingly employed capping agent, immobilizes P from sediments by altering Fe redox-coupled P cycling. Batch adsorption experiments found that LMB effectively adsorbed Fe(II) with a capacity of 8.51 mg g^{-1}. Fe(II)-preloaded LMB effectively retained P during a 518-hour equilibration, while up to 16.7% of adsorbed P was release-sensitive in LMB without Fe(II) preloading. A 60-day incubation experiment was performed using sediment cores, with an LMB amendment dosage of up to 200 LMB/P$_{mob}$ (w/w, P$_{mob}$ denotes the amount of mobile P in the surface 40 mm sediment layer). The concentrations of pore water soluble reactive P (SRP) and labile P were measured by high resolution dialysis (HR-Peeper) and by diffusive gradient in thin films (DGT), respectively, at a vertical millimeter scale. They stratified into static layers with extremely low concentration distribution in the top 16–22 mm sediments (mean SRP $\le$ 0.28 mg L^{-1} and mean DGT-labile P $\le$ 0.051 mg L^{-1}) and active layers with decreased upward diffusion potential ($\le$5.85 for SRP and $\le$12.7 for DGT-labile P) below the static layer, when the applied dosage reached 60 LMB/P$_{mob}$. The LMB amendment reduced the pore water Fe and DGT-labile Fe in sediments, while considerable amounts of Fe and Fe-bound P existed in the LMB binding layer (25% of the total P in 200 LMB/P$_{mob}$ treatment). These findings show that the adsorption of Fe by LMB plays a significant role in the stabilization of LMB-bound P, possibly by adsorbing release-sensitive P initially bound to the rhabdophane surface. LMB adsorbed Fe and P were not released until the redox potential decreased to extremely reductive conditions (−150 mV to −300 mV), possibly due to the re-adsorption of Fe and P by LMB. This study reveals synergistic effects of Fe adsorption and provides new insight into the immobilization mechanisms of P by LMB application.

1. Introduction

Processes involved in the release of internally loaded phosphorus (P) from sediments, has gained much research attention due to its usefulness in determining the trophic stage of an aquatic system (Wu et al., 2017). The application of capping agents to form an active barrier layer covering the sediment-water interface (SWI), improves the P binding capacity of sediments by allowing the association of agents with release-sensitive P (P$_{mob}$), therefore minimizing the release of P into the water column (Meis

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* Corresponding author.
E-mail address: smding@niglas.ac.cn (S. Ding).

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et al., 2012). To date, a range of capping agents have been developed and are widely applied in lakes as geoengineering tools, typically composed of high levels of aluminum, calcium, iron and other metal compounds in the form of oxides or hydroxides (Douglas et al., 2016; Fan et al., 2017; Li and Pan, 2015; Wang et al., 2017a).

A lanthanum-modified bentonite clay (LMB), commercially known as Phoslock® was developed by the Commonwealth Scientific and Industrial Research Organization (CSIRO) of Australia (US Patent No. 6350383) (Robb et al., 2003) and has shown promise for the deliberate manipulation of internal P processes in the natural environment (Douglas et al., 2016; Spears et al., 2016; Dithmer et al., 2016a). The LMB has to date been reported to be applied to more than 200 water bodies across a wide geographic distribution (Copetti et al., 2016). Immobilization efficiency of LMB can be sustained with time through the formation of rhabdophane and monazite, which have low solubility and high stability (Dithmer et al., 2015). The efficiency is less pH dependent, with a maximum efficiency within a pH range of 5–7 and a decreasing trend in efficiency above pH 9, and the adsorbed P does not release under anoxic condition (Ross et al., 2008). The number and taxa of macroinvertebrate fauna can recover from the LMB amendment after one-year application due to the shift in trophic state of the lake (Waajen et al., 2017).

Iron (Fe) is a redox-sensitive element and its redox cycle has a primary role in the control of P mobility in sediments (Ding et al., 2016a). Previous studies have mostly focused on the interactions between P and LMB, while the effects of Fe redox cycle on LMB immobilization, as yet remain unclear. It is well recognized that the immobilization of P by LMB occurs mainly by a shift of P partition in sediments from Fe bound P (i.e., bicarbonate dithionite (BD) extracted P), to La bound P (i.e., HCl extracted P) (Reitzel et al., 2013a; Meis et al., 2013; Lürling and van Oosterhout, 2013; Bishop et al., 2014). However, previous studies confirmed that not all LMB loaded P is stabilized by La binding. For instance, Meis et al. (2012) reported that 21% of SRP in LMB could be extracted by BD, confirming that a significant portion of LMB bound P is in the form of Fe- or Mn- bound P. Reitzel et al. (2013a) found that a high amount of Fe can be extracted from pure LMB by BD, which may infer that the accumulated Fe in the LMB possibly benefits the immobilization of additional P besides the LMB binding under oxic condition. Conversely, Dithmer et al. (2016b) argued that BD-extracted P was not bound to Fe or Mn oxides and is instead adsorbed to the surface of rhabdophane, as no Fe or Mn oxides were observed in LMB using ^{31}P NMR spectroscopy. As Fe oxyhydroxides are strong absorbents for P (Kumar et al., 2014), it is imperative to scrutinise the roles of Fe loading in immobilization of P by LMB. This will significantly promote our understanding of the mechanisms behind the P immobilization by LMB in the redox-sensitive sediment condition.

The purpose of this study is to establish the adsorption characteristics of Fe by LMB and its effects on P immobilization. Batch adsorption experiments were performed to investigate the kinetic and equilibrium adsorption of Fe. In addition, the adsorption characteristics of P by LMB were compared, in the presence and absence of Fe pre-loading. Sediment core incubation experiments were performed to reveal the effects of Fe adsorption on P immobilization by LMB, using high-resolution dialysis (HR-Peeper) and diffusive gradients in thin films (ZrO-Chelex DGT) sampling techniques, to simultaneously measure soluble Fe and P in pore waters and labile Fe and P in sediments.

2. Materials and methods

2.1. Materials

LMB was provided by Fusiyueke LLC (Sichuan, China). Short rod-like LMB was ground through a 2 mm pore-size mesh to ensure an even coverage of the sediment surface by LMB. All Fe $[(NH_4)_2Fe(SO_4)_2]$ and P (Na_2HPO_4) solutions were prepared using deoxygenated deionized water (Millipore, resistivity >18 MΩ cm). The HR-Peeper and ZrO-Chelex DGT probes were provided by EasySensor Ltd. (www.easysensor.net). Their principles and analyses are shown in Supplementary Materials with preparation performed according to Xu et al. (2012) and Ding et al. (2016b), respectively. HR-Peeper and DGT probes were soaked in 0.01 M NaCl and deoxygenated using nitrogen for 16 h prior to deployment in the sediment.

2.2. Batch adsorption experiment set-up

The kinetic and equilibrium adsorption of Fe^{2+} by LMB was performed by combining 0.5 mg LMB (dry weight) with 40 mL of Fe^{2+} solution, in a 50 mL centrifuge tube. The mixture was shaking for 12 h at 25 °C. In the kinetic experiment, the initial concentration of Fe^{2+} was set at 100 mg L^{-1} and the sampling time ranged from 0.6 to 240 min. In the equilibrium experiment for detection of the adsorption capacity of LMB for Fe^{2+}, the initial concentrations of Fe^{2+} ranged from 0 to 500 mg L^{-1}, and the shaking time was 24 h. The supernatants were separated after centrifugation of the mixture at 4000 rpm. The concentrations of Fe^{2+} in the supernatants were determined and the adsorption amount of Fe^{2+} was calculated. The kinetic adsorption of P by LMB was also investigated for comparison, in which the initial concentration of P in solution was set at 100 mg L^{-1}. To avoid Fe^{2+} oxygenation, all the solutions were prepared using deionized water deoxygenated with nitrogen for 16 h, and the operations were conducted in the nitrogen-purged environment.

To investigate the effects of Fe loading by LMB on the immobilization efficiency of P, 5.0 g LMB (dry weight) was transferred into 50 mL centrifuge containing 40 mL deionized water and were deoxygenated with nitrogen for 16 h. The mixture was then centrifuged at 4000 rpm for 10 min and supernatants removed. Deoxygenated LMB (1.0 g wet weight) was transferred to a 50 mL centrifuge tube containing 40 mL of either deionized water or 100 mg L^{-1} Fe^{2+} solution. The tubes were agitated on a rotary shaker at 180 rpm, 25 °C for 12 h. Supernatants were removed and 40 mL of 100 mg P L^{-1} was added to each tube and tubes were continuously agitated for 518 h. After removal of the supernatant, the exchangeable P and reducible P were extracted from the solid fraction using NH_4Cl and BD solutions, respectively.

2.3. Experimental core microcosm set-up

Sediment cores and overlying water, were collected together from the Nanfei River inlet to Lake Chaohu (117.401° N, 31.717° E), the fifth largest freshwater lake in China. Sediments were sieved through a 0.6 mm pore-size mesh to remove macrofauna and larger particles and then placed in a Perspex tube following homogenization, forming a 15 cm length sediment core. Once filtered, the overlying water was siphoned into the sediment containing tube to produce a 12 cm deep water layer. The microcosm tubes were then pre-incubated in a water bath at 25 °C for two months.

The application dose range was established as a ratio of the amount of LMB to that of mobile P (LMB/P_{mob}) and was set to be 20, 60, 100, 150, or 200 (w/w). The concentration of P_{mob} was defined as the sum of all P_{mob} in the upper 40 mm of surface sediments. For LMB amendment, LMB was combined with 500 mL of overlying water extracted from the microcosm tube, with the mixture then siphoned back into the microcosm tube to produce an even distribution of LMB on the surface of the sediment. Microcosm tubes were incubated in the water bath at 25 °C for a further two-month