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# Phosphorus fixation in lake sediments using LaCl<sub>3</sub>-modified clays

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## ABSTRACT

Fourteen types of clay, including soils and sediments from Lake Taihu, were modified by LaCl<sub>3</sub>, and their abilities of phosphorus (P) sorption (the total P up-taken) and fixation (the unleachable P retained in modified clays) were investigated. Results showed that P sorption rates of LaCl<sub>3</sub>-modified clays were all higher than 90%, while the fixation rates were raised from 3–14% to 52–95%. Kaolinite was selected to study the pH effect on P sorption and desorption of La<sup>3+</sup> from the modified clays. In the pH range of 4–8, P sorption on LaCl<sub>3</sub>-modified kaolinite could reach over 80%, with a maximum of 97% at pH 5. The desorption rate of La<sup>3+</sup> decreased with the increase of pH, which was lower than <0.006% at pH > 6.12. This study may provide a solution for internal P pollution from lake sediments.

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## 1. Introduction

Excessive phosphorus input from runoff into water bodies such as lakes, rivers, and creeks could lead to eutrophication (Smith et al., 2006; Schlusser et al., 2007). Over the last two decades, eutrophication has occurred more frequently in China, well in line with the global trend (Sivonen, 1996; Anderson, 1997; Lee et al., 1998). To date, more than 60% of the lakes in China have become eutrophic (Tiessen, 1995; Sharpley et al., 1999).

There are two sources of phosphorus for a lake or reservoir: external and internal loads. External loads come from point or non-point source pollutants, while internal loads are mostly phosphorus released from sediments through physical, chemical, or biological disturbances and processes (Dillon and Evans, 1993; Knight et al., 2003). Such internal loads contribute a significant amount of phosphorus to water bodies, even when external pollution inputs are

under control. Many attempts have been made to decrease the external P loads; however, the internal P loads from sediment release may play a substantial role in the eutrophication status of lakes (Søndergaard et al., 1999; Knight et al., 2003).

On the other hand, an environmentally friendly way to control harmful algal blooms is to use natural, non-toxic and inexpensive clays (Anderson, 1997; Pan, 1998; Sengco and Anderson, 2004), or, in a recent approach, local soils modified by chitosan (Pan et al., 2006a,b; Zou et al., 2006). However, these technologies face a common problem that the algae cells flocculated down to the lake bottom would be biodegraded in the sediments and phosphorus previously stored in the cells could be released into the water. It is necessary to find a method to permanently fix phosphorus into the modified soils/clays so that phosphorus will not be released into the water even when the sediment is re-suspended.

In this study, P fixation rates for 14 types of clays modified by lanthanum chloride were studied in a solution simulating

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the natural lake of Taihu. The effects of pH on P sorption on LaCl<sub>3</sub>-modified kaolinite and the desorption of La<sup>3+</sup> were also investigated. Results suggested that LaCl<sub>3</sub> modification of clays, soils and sediments is effective in inhibiting the release of bio-available phosphates.

## 2. Materials and methods

### 2.1. Materials

Fourteen kinds of clays used in the experiments were prepared by drying at 100 °C and sieving through 180 meshes (74 μm). The characteristics of the clays were measured and displayed in Table 1. Lanthanum chloride (LaCl<sub>3</sub>) used was of chemical reagent (A.R.) grade. All other chemicals used were of analytical grade.

### 2.2. Methods

#### 2.2.1. Preparation of the modified clays using LaCl<sub>3</sub>

Ten grams of clay was added into 500 mL of 2% (w/w) LaCl<sub>3</sub> solution (initial pH 8.3). The mixture was shaken for 48 h at 20 °C and placed into a pressure apparatus at 2 kPa for 1 h. After this, the sample was filtered through a 0.45 μm membrane and the residue was washed with deionized water 3–5 times (Wasay et al., 1996). The residue was placed in the oven at 60 °C for 12 h, and then into a dryer. Finally, the modified clays were dried at 100 °C and sieved through 180 meshes with the particle size less than 74 μm.

#### 2.2.2. Measurement of phosphorus sorption

A solution of 1 mgL<sup>-1</sup> phosphorous was prepared using analytical-grade potassium dihydrogen phosphate. A solution containing 30 mL of the above-mentioned solution was taken into a polycarbonate tube. The clay (0.1800 g) was added into each tube and the pH was adjusted to 7.50 by drop-wise addition of dilute HCl or NaOH solution. The mixture was shaken at 25 °C, 150 rpm for 24 h. After 24 h of equilibration, the clay was removed by centrifugation and P concentration of supernatant

was measured by the UV-vis spectrophotometer at λ = 700 nm (SEPA, 2002). Each experiment was carried out in triplicate and the average results are presented in this study. The sorption capacity and rate are defined as:

$$\text{Sorption capacity } (\mu\text{g g}^{-1}) = \frac{V \times (C_i - C_f)}{m}$$

$$\text{Sorption rate } (\%) = \frac{\text{Sorption capacity} \times m}{V \times (C_f - C_e)} \times 100$$

where *m* (g) is the mass of the clay, *V* (mL) is the volume of P solution, and *C<sub>i</sub>* and *C<sub>f</sub>* (mgL<sup>-1</sup>) are initial and final P concentration, respectively.

#### 2.2.3. Measurement of P fixation (Olsen method)

The above-mentioned solution was filtrated, and the residue on the filter paper was washed by deionized water 3–5 times. After 12 h, the residue and the filter paper were placed into a flask. 50 mL NaHCO<sub>3</sub> (0.5 molL<sup>-1</sup>, pH 8.5) was added into the flask and shaken for 30 min. Other analytical procedures were the same as those described in Section 2.2.2. The fixation capacity and rate are defined as:

$$\text{Fixation capacity } (\mu\text{g g}^{-1})$$

$$= \text{Sorption capacity} - \text{APs in the solution (Olsen method)}$$

$$\text{Fixation rate } (\%) = \frac{\text{Fixation capacity} \times m}{V \times (C_i - C_f)} \times 100$$

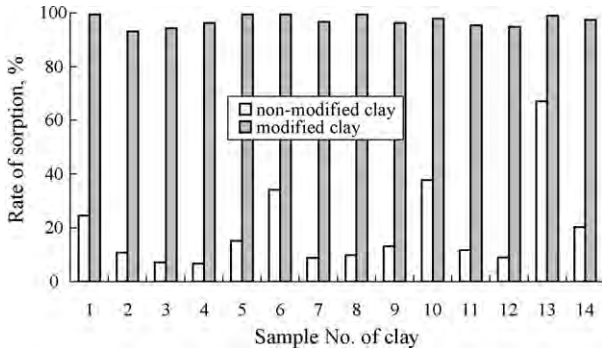
#### 2.2.4. The effect of pH on P sorption and La<sup>3+</sup> release from the modified clays

Under a similar condition described in Section 2.2.2, different pH values of the solutions were adjusted using HCl or NaOH solutions. The pH values were measured as the final pH after the solutions were shaken for 3 days. The mixture was centrifuged and La<sup>3+</sup> in the supernatant was analyzed by the ICP-OES (OPTIMA 2000, PerkinElmer Co., U.S.A.).

**Table 1 – Characterization of the clay/minerals, soils and sediments**

Sample no.	Clay	Specific gravity (g cm <sup>-3</sup> )	Particle size (μm)	
			Volume weighted average	Mode
1	Volcanic scoria	2.7–2.84	42.3	56.4
2	Porcelain clay	2.6–2.8	43.4	42.8
3	Pumice II	2.3–2.4	26.0	56.4
4	Argil	2.6–2.8	20.9	40.2
5	Clinoptilolite	2.16	30.6	49.1
6	Laterite	2.75–3.0	10.7	4.1
7	Mica	2.7–3.5	65.0	74.3
8	Argillaceous rocks	2.23–2.28	26.5	49.1
9	Pumice I	2.7–2.84	14.3	10.1
10	Attapulgit (70%) <sup>a</sup>	2.05–2.3	26.6	32.4
11	Illite (65%)	2.6–2.9	20.7	4.7
12	Kaolinite (80%)	2.6–2.63	7.4	9.4
13	Sediments of Taihu	2.5–2.8		
14	Soils	2.6–3.0		

<sup>a</sup> The purities of clays are shown in brackets.

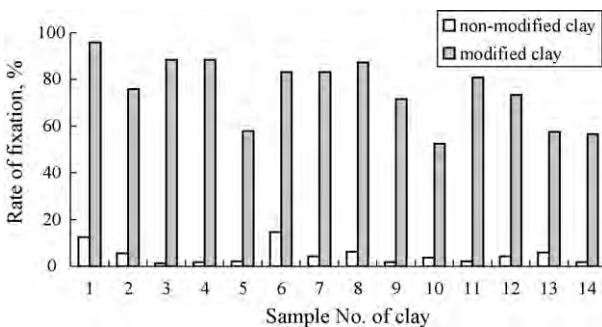


**Fig. 1 – P sorption rates of unmodified clays and LaCl<sub>3</sub>-modified clays.**

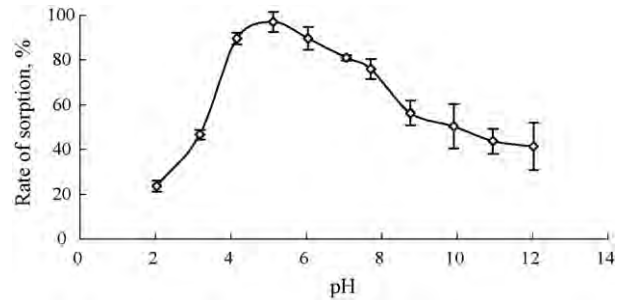
### 3. Results and discussion

P sorption rates of unmodified clays and LaCl<sub>3</sub>-modified clays in 1 mgL<sup>-1</sup> P solution are shown in Fig. 1. P sorption rates of unmodified clays were much lower than those of LaCl<sub>3</sub>-modified clays. The sediments from Meiliang Bay of Lake Taihu had the highest P sorption rate of 67%, and the P sorption rates of other unmodified clays were only 6–37%. The P sorption rates of LaCl<sub>3</sub>-modified clays were significantly increased to 93–99%, more than double that of the previous values. For example, the P sorption rate of modified Pumice II (No. 3) was 94.24%, 12 times higher than that of the unmodified ones, and that of the modified Argil (No. 4) was 96.34%, 13 times higher than that of the unmodified ones.

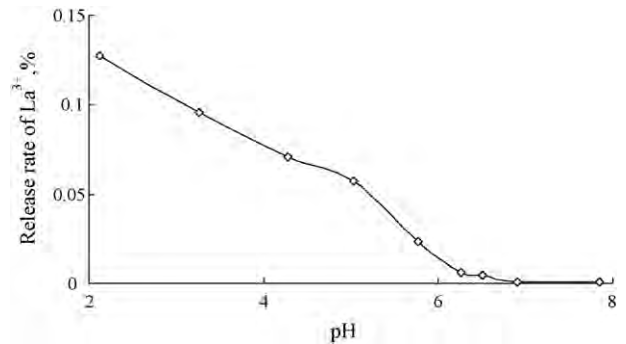
The P fixation rates of unmodified clays and LaCl<sub>3</sub>-modified clays are shown in Fig. 2. The fixation rates of unmodified clays were 3.78–14.69%, only 1/3–1/2 of their sorption rates, indicating that the unmodified clays not only had lower sorption rates, but also lower fixation rates. In contrast, the LaCl<sub>3</sub>-modified clays showed both high P fixation rates (52.43–95.78%) and high P sorption rates (Fig. 1), suggesting that the phosphorus sorbed on unmodified clay could release easily into the solutions in the actual re-suspension process of the lake sediments, but the LaCl<sub>3</sub>-modified clays might inhibit the P release remarkably. In comparison, the fixation rate of LaCl<sub>3</sub>-modified Attapulgit (No. 10) was 52.43%, the lowest in all the 14 types of modified clays, but it was still much higher than that of the unmodified one of 3.78%. The fixation rate of Laterite (No. 6) was 14.7%, highest among all the unmodified clays, much lower than that of LaCl<sub>3</sub>-modified ones. Therefore



**Fig. 2 – P fixation rates of unmodified clays and LaCl<sub>3</sub>-modified clays.**



**Fig. 3 – Effect of pH on P sorption rate of LaCl<sub>3</sub>-modified kaolinite.**



**Fig. 4 – Effect of pH on La<sup>3+</sup> release in solution.**

the LaCl<sub>3</sub>-modified clays had a strong ability for P sorption and fixation, and could help solve the P release problems caused by re-suspension of lake sediments.

P sorption rates of LaCl<sub>3</sub>-modified kaolinite at different initial pH values are presented in Fig. 3. The P sorption rate of modified kaolinite was greater than 80% in the pH of 4.0–7.3, and reached a maximum of 97% at pH 5. The P sorption rate of modified kaolinite decreased from 97% to 24% with decreasing pH from 5 to 2, and decreased to 41% when pH increased from 5 to 12. The reason P sorption had a peak around pH, 5 is partly because at this pH phosphate is almost in the form of H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. When the solution pH is lower than 5, the available surface hydroxyls may decrease with pH, resulting in the decrease of P sorption of modified kaolinite. There are two explanations for the decrease of P sorption rate with pH increasing from 5 to 12. On one hand, the interactions of static sorption between phosphate and the modified kaolinite is weakened while the surface charge decreases with the increase of solution pH. On the other hand, the OH<sup>-</sup> concentration increases with increasing pH, which competes directly with H<sub>2</sub>PO<sub>4</sub><sup>-</sup> in sorption onto the surfaces of modified kaolinite (Ding et al., 2003; Wu, 2004; Shin et al., 2005).

Fig. 4 shows that La<sup>3+</sup> desorption from the LaCl<sub>3</sub>-modified kaolinite decreased with increasing pH in the range of 2–8. The desorption rate of La<sup>3+</sup> was 0.13% at pH 2.2, 0.006% at pH 6.1, and reached a minimum of 0.0007% at pH 7.85. Dissolved La<sup>3+</sup> released from the LaCl<sub>3</sub>-modified clays was below detection limit at pH 8.5. For fresh water media, carbon dioxide is a key factor to maintain the pH in the lake. The pH will increase as carbon dioxide is removed from the water during photosynthesis by the growing algae. Thus, during algal blooms when

the water bodies tend to be more alkaline. The  $\text{LaCl}_3$  modification method could be used stably to control internal P pollution in lake sediments.

#### 4. Conclusions

- (1)  $\text{LaCl}_3$ -modified clays had a strong ability for increasing both P sorption and P fixation, as compared to the unmodified ones. The sorption rates of modified clays were in the range of 93.18–99.44% while those of unmodified clays were only 6.75–37.70%. The fixation rate of modified clays was in the range of 52–96%, much higher than 4–15% of the unmodified ones.
- (2) The P sorption rates on  $\text{LaCl}_3$ -modified clays were pH-dependent. The P sorption rate of modified kaolinite was greater than 80% in the initial pH range of 4–8, and reached a maximum of 97% at pH 5.
- (3) The  $\text{La}^{3+}$  desorption rate decreased with increasing pH, and the modified clays had little  $\text{La}^{3+}$  released in the pH range of natural water bodies especially during the algae blooms.  $\text{LaCl}_3$ -modified clays, soils and sediments would be helpful in controlling internal P pollution in lake sediments.

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