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Interactions of phosphate and dissolved organic carbon with lanthanum modified bentonite: Implications for the inactivation of phosphorus in lakes

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ABSTRACT

Lanthanum-modified bentonite (LMB) is a widely used phosphorus-inactivating agent in lakes. However, dissolved organic carbon (DOC) exists ubiquitously in lakes, and its influence on phosphate binding is still not adequately understood. Our results showed that both phosphate and DOC can be adsorbed by LMB. The Langmuir adsorption maxima of phosphate and DOC were 9.06 mg P/g and 5.31 mg C/g, respectively, generating a C/P molar ratio ~1.5. When phosphate and DOC coexisted at this ratio, the adsorption of phosphate was not influenced by DOC and vice versa. However, the phosphate capture by LMB was significantly reduced by raising the ratio above ~9, and the reduction was increased with increasing the ratio. Once adsorbed by LMB, phosphate was essentially not desorbed by DOC, while adsorbed DOC can be mostly liberated by phosphate. It is deemed that phosphate can interact preferentially with La on LMB. However, DOC can still be adsorbed by LMB, even after LMB was saturated with phosphate, which was attributed to (i) the high coordination capacity of La; (ii) the interaction of DOC with the hydroxyl group(s) of the adsorbed phosphate via hydrogen bonding; and (iii) the interaction of DOC with the La sites unoccupied by phosphate. We proposed that LMB can be applied in the season (time) when the DOC/P ratio in lakes is low enough to facilitate the adsorption of phosphate, which will no longer be released into water, even after the C/P ratio is raised later.

1. Introduction

Phosphorus inactivation agents (PIAs) have been utilized for about half a century to suppress the internal phosphorus loading in eutrophic lakes (Douglas et al., 2016). The early PIAs were soluble metal salts, and, among them, alum has been used for phosphorus and algae control in more than 200 lakes, especially in lakes of North America and Europe (Jensen et al., 2015; Welch, 2005).

Although the application of soluble metal salts, particularly alum, is still one of the most effective measures for the control of the internal phosphorus loading in deep-water lakes, the use of insoluble solid PIAs has attracted increasing attention in recent years (Berg et al., 2004; Copetti et al., 2015; Gibbs et al., 2011; Lin et al., 2019; Lürling et al., 2016; Wang and Jiang, 2016; Wang et al., 2017, 2019). The lanthanum-modified bentonite (LMB) developed by the Australian Commonwealth Scientific and Industrial Research Organization (CSIRO) is the most investigated solid PIA and has been shown to be very promising for lake restoration (Copetti et al., 2015; Dithmer et al., 2015; Egemose et al., 2010; Lürling and Faassen, 2012; Lürling and Tolman, 2010; Mucci et al., 2018; Reitzel et al., 2013; Ross et al., 2008; Spears et al., 2016; Waajen et al., 2016; Yin et al., 2018). It has been successfully used in approximately 200 water bodies for large-scale practical applications (Copetti et al., 2015). The main advantages of this PIA can be summarized as follows: i) LMB exhibits an excellent efficiency. Lanthanum has a high affinity for phosphate, and the solubility of the formed lanthanum phosphate product is the lowest among rare earth elements (Firschlng and Brune, 1991). In addition, the coordination capacity of lanthanum is strong. For example, the characteristic coordination number of iron and aluminium is 6, while that of lanthanum can reach 12 (Wu et al., 2007). ii) The inactivated product exhibits a high stability. Unlike other PIAs, the interaction of phosphate with LMB produces rhabdophane minerals ($LaPO_4 \bullet nH_2O$) (Dithmer et al., 2015), which is highly stable under the common pH range and redox conditions found in natural waters (Copetti et al., 2015). iii) LMB is ecologically safe. Ecological

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impact tests show that LMB is safe for aquatic life (Lürling and Tolman, 2010). To date, there have been no indications of the long-term negative impact of using LMB on the ecosystem (Spears et al., 2016). iv) LMB is cost-effective. Lanthanum is not only the most abundant among the rare earth elements but also the cheapest (Taylor and McClennan, 1985). Taking Rauwbraken Lake in the Netherlands as an example, the cost of using LMB to control the endogenous phosphorus load in the lake is estimated to be only one tenth of the cost of dredging (Lürling and Faassen, 2012).

Assuming that $LaPO_4 \bullet nH_2O$ was formed, the theoretical binding ratio for lanthanum and phosphate is 1:1. However, it has been widely reported that the removal of phosphate by LMB was not proportional, and the interference from the water parameters was thus documented (Egemose et al., 2010; Lürling and Faassen, 2012; Reitzel et al., 2013; Ross et al., 2008; Wang et al., 2017). For instance, a negative relationship between alkalinity and the phosphate binding capacity of LMB was observed and the higher phosphate binding capacity of LMB in lakes with lower alkalinity could be attributed to a more pronounced dispersion of LMB (Reitzel et al., 2013, 2017). Dissolved organic carbon (DOC) is another important water parameter to influence the binding of phosphate by LMB (Dithmer et al., 2016; Lürling et al., 2014; Spears et al., 2016). DOC exists ubiquitously in lake water and in the pore water of lake sediments (De Lange, 2000; de Vicente et al., 2008). In particular, eutrophic lakes tend to have higher DOC concentrations (on average, 10–30 mg/L) than oligo/mesotrophic lakes (on average, 2–3 mg/L) (Li et al., 2019; Thurman, 1985). Furthermore, DOC is often found in higher concentrations in pore water compared to lake water (Dithmer et al., 2016). LMB is usually applied to the surface lake water, where it can capture dissolved phosphorus and, once settled onto the surface of the sediment bed, LMB can inactivate the phosphorus in sediment by sequestering phosphorus from the pore water. Hence, the effect of DOC on the efficacy of LMB for eutrophication control is of the utmost importance.

The work by Lürling et al. (Lürling et al., 2014) was the first study to understand the influence of DOC, and their results showed that less phosphate was removed in the presence of humic substances. Laboratory tests by Dithmer et al. (Dithmer et al., 2016) also revealed the negative effects of two model DOC compounds, humic acid and phthalate, on the phosphate binding capacity of LMB. Furthermore, using lake water samples from 16 Danish lakes, a significant negative relationship was found between the natural DOC concentration (and colour) and the phosphate binding capacity of LMB. Similarly, Spears et al. (Spears et al., 2016) examined the effectiveness of LMB across a wide range of lake conditions and found that the phosphorus concentrations following LMB applications varied across the lakes and were correlated positively with the DOC concentrations, indicating that DOC interfered with the phosphorus removal by LMB. However, the effect of DOC on the phosphate adsorption by LMB is still not adequately clarified. For instance, although the maximum adsorption capacity of phosphate by LMB can be expressed by the La/P molar ratio of 1:1 because the formation of $LaPO_4 \bullet nH_2O$ was confirmed, the maximum adsorption capacity of DOC by LMB has still not been measured before. In other words, the ratio of the adsorption maxima of DOC versus phosphate (C/P molar ratio or C/La molar ratio) is still unknown. Understanding the adsorption behaviour of DOC by LMB would help determine how DOC influences phosphate adsorption by LMB. In addition, although the removal of phosphate by LMB in the presence (at different concentrations) and absence of DOC was investigated previously and negative effect of DOC on phosphate removal was shown (Dithmer et al., 2016; Lürling et al., 2014), the experiments were done when phosphate and DOC coexisted. It is still not clarified if phosphate previously adsorbed on LMB is stable when exposed to DOC later and if DOC previously adsorbed on LMB is stable when exposed to phosphate later. This information is important to understand, for the binding of phosphate and DOC by LMB, which solute has higher affinity towards the adsorption sites, and which solute can be more strongly retained by LMB.

In this study, to better understand the efficacy of LMB for phosphate removal in the presence of DOC, the adsorption behaviours of both phosphate and DOC were first evaluated. Second, the phosphate immobilization by LMB was examined as a function of the DOC concentration in both deionized water and DOC-spiked lake water taken from Lake Taihu, which is located in the Yangtze Delta Plain and is the third largest freshwater lake in China. Lake Taihu has an area of 2250 km^2 and an average depth of 2 m. Third, the reversibility of the adsorption of both phosphate and DOC on LMB was determined. Finally, the implication of the results for the inactivation of phosphorus in lakes was discussed.

2. Materials and methods

2.1. Materials

The LMB sample used in this study was provided by the Shanghai Phoslock Water Solutions Ltd. For comparison purposes, a natural bentonite sample was obtained from the Linshou Hengchang Mining Co., Ltd., Hebei Province, China. The samples were ground to pass through an 80-mesh sieve prior to use. The chemical composition of bentonite and LMB are presented in Table 1. The elemental compositions of the materials were determined by X-ray fluorescence (Axios X, PANalytical Company), while the moisture and loss on ignition were measured from the weight loss at 105 °C and 900 °C, respectively.

The phosphate solutions were prepared with KH_2PO_4. Humic acid has been widely used as a model DOC compound and was also used in this study. Humic acid was supplied by Aldrich Chemical in the form of humic acid sodium salt, which was extracted from waters draining from an open pit mine in Oberhessen, Germany.

The natural lake water sample was obtained on August 24th, 2018 from the Gonghu Bay of Lake Taihu (31°21′23″N, 119°59′35″E). The concentrations of some of the soluble components are given in Table S1. Among them, the total P and soluble reactive P (SRP) concentrations were determined using the molybdenum blue colorimetric method (Chinese Environmental Protection Administration, 2002). DOC was measured using a CHNOS elemental analyser (model Vario ELIII, Germany) after the water had been filtered through a 0.45 μm membrane filter. The total alkalinity (in $CaCO_3$) was determined to be 87.8 mg/L by the titration method (Chinese Environmental Protection Administration,

Table 1
Chemical compositions of bentonite and LMB (%).

Item	Bentonite	LMB
SiO_2	71.70	64.15
Al_2O_3	13.93	16.08
Fe_2O_3	2.32	3.43
CaO	0.08	4.05
MgO	3.11	3.45
Na_2O	8.20	0.58
K_2O	0.28	1.22
TiO_2	0.15	0.33
ZrO_2	0.02	0.07
La_2O_3	N.D.[a]	5.86
Moisture	10.23	7.86
LOI[b]	4.38	8.63

[a] Not detectable.
[b] Loss on ignition.

2002). All other common ions were determined by inductively coupled plasma-atomic emission spectroscopy (ICAP 6000 Radial, Thermo, USA) and ion chromatography (METROHM, MICI, Switzerland). The water sample had a pH of 7.5, as measured by a Hach Sension + pH meter.

2.2. Methods

2.2.1. Adsorption isotherm studies

The adsorption isotherm experiments were conducted using aqueous solutions containing either phosphate or DOC. The initial phosphate and DOC concentrations ranged from 5 to 100 mg/L and from 2.5 to 300 mg/L, respectively. All the solutions contained 0.01 M NaCl as the background electrolyte. First, stock solutions of KH_2PO_4 with the concentration of 1000 mgP/L and humic acid sodium salt with the concentration of 1000 mgC/L were separately prepared using 0.01 M NaCl solution. The working solutions of phosphate and DOC were then obtained by dilution of the stock solutions with 0.01 M NaCl solution. The use of 0.01 M NaCl was to keep the ionic strength roughly constant, independently of the amount of KH_2PO_4 or humic acid sodium salt added. The experiments were performed by adding 40 ml of the aqueous solutions to centrifuge tubes containing 0.1 g of LMB or the bentonite sample. The tubes were then shaken at 180 rpm and 25 °C for 48 h. An adsorption time of 48 h was found to be sufficient for both phosphate and DOC to achieve equilibrium in our adsorption kinetics studies (Fig. S1). Specifically, under our experimental conditions, the amount of adsorbed phosphate and DOC increased sharply at the initial stage and then continued to increase slowly, but the adsorption amount reached equilibrium at 24 h, since there was no statistically significant increase in the amount adsorbed between the adsorption time of 24 h and 48 h (Duncan multiple comparisons, $p > 0.05$). After 48 h, the suspensions were centrifuged, and the phosphate concentrations in the supernatants were determined by the molybdenum blue-ascorbic acid method (Chinese Environmental Protection Administration, 2002), and DOC was evaluated directly at a wavelength of 218.5 nm with a Unico spectrophotometer (Model UV-2102PCS, China). The amount of adsorbed phosphate or DOC at equilibrium (q_e) was calculated using the following equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{1}$$

where V is the volume of the solution (L), C_0 and C_e are the initial and equilibrium concentrations of phosphate or DOC (mg/L), respectively, and m is the dry mass of LMB or bentonite (g).

Adsorption isotherm experiments using aqueous solutions containing both phosphate and DOC were also carried out. In this case, the phosphate concentration varied from 5 to 100 mg/L, while the DOC concentration was set to achieve a constant C/P molar ratio of 1.5:1. This ratio was adopted since the C/P molar ratio when the adsorption capacity of phosphate and DOC on LMB attained saturation was ~1.5:1. The DOC concentration in the supernatant was directly measured spectrophotometrically, while the phosphate concentration was determined after the supernatant was digested with a potassium persulfate solution, because our preliminary experiment confirmed that the colour of DOC can influence the quantification of phosphate when the DOC concentration exceeded ~20 mg/L.

2.2.2. Adsorption of phosphate as a function of the DOC concentration

Forty millilitres of a phosphate solution with different DOC concentrations was added to 50 ml centrifuge tubes containing 2.48 mg of LMB. This dose corresponds to the LMB/P mass ratio of 100:1 which was used in previous studies (Dithmer et al., 2016; Lürling et al., 2014; Reitzel et al., 2013; Waajen et al., 2016; Yin et al., 2018). To accurately add small amount of LMB, a stock suspension was first prepared by the continuous mixing of 2.48 g of LMB with 1 L of deionized water. Subsamples of 1 mL were taken from this suspension and were transferred to centrifuge tubes. The phosphate concentration of 0.62 mg/L was adopted, as it is representative of the pore water concentrations in Danish eutrophic lakes (Reitzel et al., 2013). The DOC concentration was set to 0, 0.5, 2, 4, 8, 12, 20, 40, 60, 80, and 120 mg/L. This range of DOC concentrations can represent the natural DOC concentration level in Danish lakes (de Vicente et al., 2008; Dithmer et al., 2016). Furthermore, the solutions were prepared with a 0.01 M ammonium chloride-ammonia buffer solution instead of pure water to achieve a constant pH of 7.5 and an ionic strength equal to that of 0.01 M NaCl. After being shaken at 25 °C and 180 rpm for 48 h, the mixture was filtered through a 0.45 μm cellulose acetate membrane filter, and the filtrate was then digested with a potassium persulfate solution. The phosphate concentration in the digested filtrate was measured.

2.2.3. Adsorption of phosphate from natural lake water spiked with DOC

Before the experiment, the lake water was spiked with KH_2PO_4 to achieve an SRP concentration of ~0.62 mg/L. Furthermore, an aliquot of this lake water was spiked with humic acid to achieve a DOC concentration of 14.21 mg/L, i.e., increasing the DOC concentration by 10 mg/L. Forty millilitres of the lake water with or without the adjusted DOC concentration was added to 50 ml centrifuge tubes, and 2.48 mg of LMB was added. For comparison purposes, experiments using a phosphate solution with a concentration of 0.62 mg/L, which was prepared from pure water, were also conducted. The tubes were shaken at 25 °C and 180 rpm. After 1, 2, 4, 8, 14, 20, and 28 days, the suspensions were filtered through a 0.45 μm membrane filter, and the SRP concentration of the filtrates were determined.

2.2.4. Reversibility of phosphate and DOC adsorption

To evaluate the reversibility of phosphate adsorption, the first step was to prepare phosphate-loaded LMB. For this purpose, 0.1 g of LMB was weighed and placed in 50 ml centrifuge tubes. Then, 40 ml of a phosphate solution whose concentration was 50 mg/L was added. This phosphate concentration was adopted to reach nearly the maximum amount of phosphate adsorption based on the isotherm studies. The solution contained 0.01 M NaCl as the background electrolyte. After being shaken at 25 °C and 180 rpm for 48 h, the tubes were centrifuged, and the phosphate concentration and amount of phosphate adsorbed by LMB (q_e) were calculated with the supernatants. The solid in the tube was rinsed five times with deionized water to remove any residual phosphate that was not adsorbed by LMB.

The second step was to measure the adsorption isotherm of DOC on the phosphate-loaded LMB, which was performed according to the method described in section 2.2.1. However, the phosphate concentration in the equilibrium solution was additionally measured, and the amount of phosphate desorbed from LMB (q_d) was calculated as follows:

$$q_d = \frac{C_d \times V}{m} \tag{2}$$

The desorption efficiency was calculated using the following equation:

$$\eta' = \frac{q_d}{q_e} \times 100\% \tag{3}$$

where C_d is the phosphate concentration in the supernatant after desorption (mg/L), V is the volume of the DOC solution added as the desorption reagent (L), and q_e is the amount of phosphate adsorbed (mg/g).

To further illustrate the reversibility of phosphate adsorption, the phosphate-loaded LMB was also repeatedly washed with the DOC solution. That is, the DOC solution, which had a concentration of 50 mg/L and used 0.01 M NaCl as the background electrolyte, was added to the tubes containing phosphate-loaded LMB. This DOC concentration was used because DOC can nearly reach its maximum adsorption amount based on the isotherm studies. The tubes were shaken at 25 °C and 180 rpm for 48 h to desorb the adsorbed phosphate. After centrifugation, the phosphate concentration in the supernatant was measured. After this desorption step, a fresh DOC solution was again added, and the desorption experiment was repeated three times in total.

The reversibility of DOC adsorption was evaluated in the same manner by measuring the desorption of DOC previously adsorbed on LMB and using the phosphate solution as the desorption agent.

2.2.5. Data analysis

The phosphate and DOC concentrations were expressed in elemental P and C, respectively. All the experiments were undertaken in triplicate, and the mean value and the standard deviation are reported. Whenever necessary, data were also analysed using one-way analysis of variance by comparing the treated groups and the control and/or comparing the different treated groups using the Student-Newman-Keuls multiple range tests. The homogeneity of variance was tested using Bartlett's test. The statistical analysis was performed using the Statistical Analysis System (SAS 8.2; SAS Institute, Cary, NC, USA). All the significance levels mentioned in the text are $p < 0.05$.

3. Results and discussion

3.1. Adsorption isotherms

The results of the separate adsorption isotherms of phosphate and DOC on LMB and a bentonite sample are presented in Fig. 1a. The affinity of LMB for phosphate was high, causing a vertical isotherm shape at the low initial phosphate concentrations. This means that, at low phosphate concentrations, LMB can exhaust or uptake most of the phosphate in the water, leaving a very low residual phosphate concentration. Specifically, when the initial phosphate concentration was lower than 10 mg/L, >99% of the phosphate in the water can be sequestered by LMB. The results in Fig. 1a also showed that LMB has the capability to adsorb DOC. However, it appeared that the affinity of LMB for DOC was lower than that of LMB for phosphate, since only ~40% of the DOC in the water can be captured by LMB, even when the DOC concentration was low (<30 mg/L). The complex formation of La with humic substances was previously predicted at 5 mg/L (Tang and Johannesson, 2003) and experimentally demonstrated, for example, at 10 mg/L (Sonke and Salters, 2006; Tang and Johannesson, 2003, 2010). Our results suggested that the fixation of DOC by the La on LMB can occur at a concentration as low as 2.5 mg/L (removal efficiency ~40%).

At high concentrations, however, the amount of both phosphate and DOC adsorbed by LMB levelled off, indicating that the adsorption sites are limited, and the adsorption ability reached saturation. Nevertheless, as seen in Fig. 1a, the bentonite sample exhibited a very low adsorption capacity for both phosphate and DOC. This is expected, however, since both the bentonite surface, the phosphate ion and DOC are negatively charged, and repulsion between the bentonite surface and the two adsorbate species must take place. Therefore, although the bentonite sample used in this study is different from that used for the preparation of LMB (the latter bentonite is not available), it is reasonable to conclude that both phosphate and DOC are fixed by the lanthanum on LMB.

The adsorption isotherm data were fitted using the common Langmuir and Freundlich models, which were given below:

$$\text{Langmuir model: } Q_e = Q_{\max} K_L \frac{C_e}{1 + K_L C_e} \tag{4}$$

$$\text{Freundlich model: } Q_e = K_F C_e^{1/n} \tag{5}$$

where C_e is the adsorbate concentration at equilibrium (mg/L); K_L is a Langmuir constant related to the affinity of the binding sites (L/mg); Q_{max} is the maximum adsorption capacity (mg/g); K_F is a Freundlich constant related to the adsorption capacity ((mg/g)/(mg/L)$^{1/n}$); and $1/n$ is a constant related to the adsorption density.

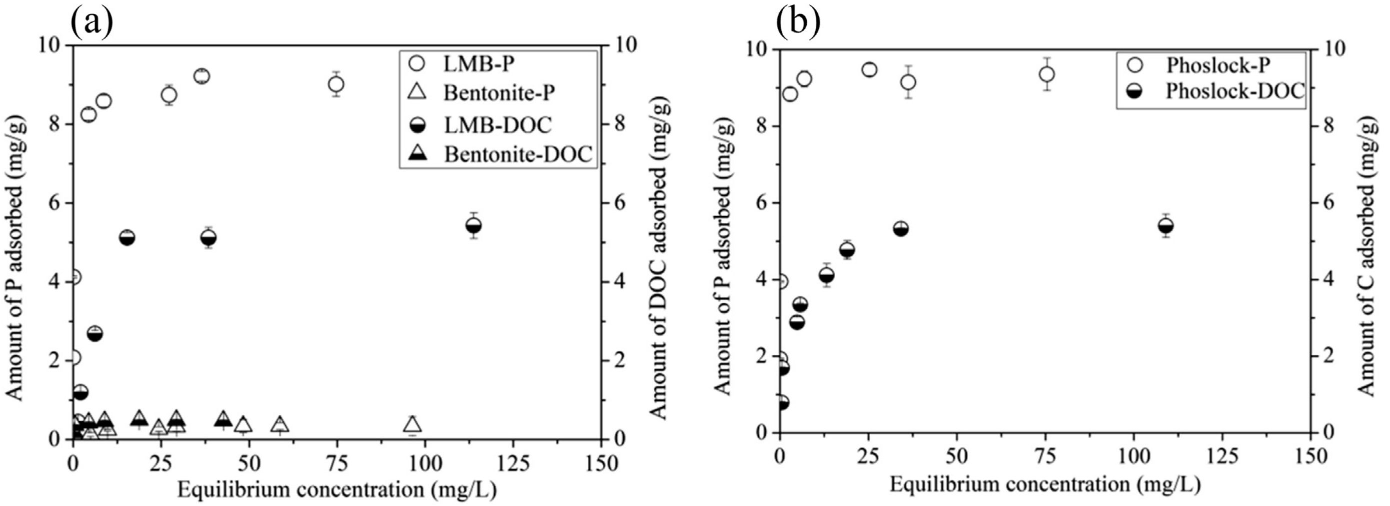

Fig. 1. Adsorption isotherms of phosphate and DOC on the materials. Left: separate adsorption of phosphate and DOC; right: co-adsorption of phosphate and DOC. The presented data are the mean values and standard deviations of triplicate experiments.

The fitting results are given in Table 2. From the correlation coefficients (R^2 values), it can be concluded that the Langmuir model gave a better fit than the Freundlich model, with R^2 values all exceeding 0.995. From the Q_{max} value of phosphate shown in Table 2 and the La content of LMB shown in Table 1, the La/P molar ratio was estimated to be 1.23:1, which was slightly higher than the 1:1 binding ratio theoretically determined by assuming that $LaPO_4 \bullet nH_2O$ formed, meaning that a small part of La was not available for phosphate binding.

The lanthanum speciation depends on the hydrolysis of the La ion. Because the pH condition used in this study was not regulated and was measured to be 7.3 ± 0.4, the dominant La species would be mostly trivalent La ions (La^{3+}) with a small proportion of divalent hydroxyl La ions ($LaOH^{2+}$), while the existence of the species $La(OH)_2^+$, $La(OH)_3$ and $La(OH)_4^-$ is unlikely (Kawahigashi et al., 2005). On the other hand, the predominant phosphate species at a pH 7.3 ± 0.4 would be a mixture of $H_2PO_4^-$ and HPO_4^-, because these two species are exclusively present at pH values ranging from 5 to 10 (Bouyer et al., 2006). Therefore, the surface species present due to the inner-sphere complex formation of phosphate with LMB can be inferred as follows (Guan et al., 2020):

$$\equiv La + HPO_4^{2-} \leftrightarrow \equiv La{-}HPO_4 \tag{6}$$

$$\equiv La + H_2PO_4^- \leftrightarrow \equiv La{-}H_2PO_4 \tag{7}$$

$$\equiv La{-}OH + HPO_4^{2-} \leftrightarrow \equiv La{-}PO_4 + H_2O \tag{8}$$

$$\equiv La{-}OH + H_2PO_4^- \leftrightarrow \equiv La{-}HPO_4 + H_2O \tag{9}$$

From the Q_{max} values of phosphate and DOC, it was calculated that the adsorption capacity of phosphate and DOC had a C/P molar ratio of ~1.5:1 when their adsorption reached saturation. Compared with the small inorganic phosphate anion, which can come close to the surface for binding, the size of DOC macromolecules is large. For instance, the diameter of humic acid is approximately 2–7 nm (Rahnemaie et al., 2007). Therefore, although most of the phosphate ions can be bound to La, a large part of the DOC has to be positioned beyond the adsorption sites, and only a small part of the carboxylate groups ($RCOO^-$) can interact with La to form an inner sphere complex, according to the ligand exchange reaction similar to that occurring for phosphate (Hiemstra et al., 2013; Weng et al., 2012):

$$\equiv La + RCOO^- \rightarrow \equiv La{—}OOCR \tag{10}$$

$$\equiv La{-}OH + RCOOH \rightarrow \equiv La{—}OOCR + H_2O \tag{11}$$

3.2. Co-adsorption of phosphate and DOC

The results of the co-adsorption isotherms of phosphate and DOC coexisting in water at a C/P molar ratio of 1.5:1 are given in Fig. 1b, and the fitting results of the adsorption isotherm data to the two adsorption models are listed in Table 2. It can be seen that the adsorption of both phosphate and DOC was essentially not influenced by one another, and their adsorption maxima differed little from their adsorption maxima obtained when they presented in water as a single adsorbate. This phenomenon was surprising and may be explained by the great coordination capacity of La. Although both the solutes can be coordinated with La, the small phosphate ion would be more competitive than DOC (this will be described in more detail in section 3.4) and would interact first with La. However, even after phosphate was adsorbed, the characteristic coordination number of 12 for La still renders the adsorption of DOC possible. In addition, the interaction of the abundant O, N and S atoms of DOC with the hydroxyl group of the phosphate adsorbed via hydrogen bonding may also contribute to the adsorption of DOC after phosphate adsorption. One more explanation is that phosphate did not occupy all the La sites (as abovementioned, the La/P molar ratio was 1.23:1, which was larger than 1:1) and the interaction of DOC with these unoccupied La sites scattered on the bentonite surface may be still possible. In this case, due to the large size of DOC, the interaction of each carboxyl group can add adsorption forces to the DOC macromolecule, rendering the adsorption of large DOC particles possible. In each case, however, the hydrogen bonds can occur both intra- and inter-molecularly between the adsorbed DOC, which would certainly facilitate adsorption.

3.3. Adsorption of phosphate in the presence of DOC at different C/P molar ratios

As abovementioned, the adsorption of phosphate was not influenced by the presence of DOC (and vice versa) at the low C/P molar ratio of 1.5:1, which was relevant to the ratio of their Q_{max} values. However, it should be noted that the C/P molar ratio in natural lakes would be much higher. For instance, Dithmer et al. (Dithmer et al., 2016) measured the SRP and DOC concentrations in both lake water and sediment pore water obtained from 16 Danish lakes and found that the C/P molar ratio in the lake water and pore water was as high as 165 and 70, on average, respectively. Even assuming that the phosphorus concentration reached 0.62 mg/L, which is the representative phosphorus concentration level in the pore water of sediments of eutrophic lakes (Reitzel et al., 2013), the

Table 2
Parameters of the Langmuir and the Freundlich models for the adsorption of phosphate and DOC on the materials studied.

Material	Solute	Langmuir model			Freundlich model		
		Q_m (mg/g)	K_L (L/mg)	R^2	n ((mg/g)/(mg/L)$^{1/n}$)	K_F	R^2
LMB	P	9.06	3.91	0.9997	6.11	5.31	0.8827
LMB	P (+DOC)	9.35	5.74	0.9999	4.92	4.98	0.8285
LMB	DOC	5.31	0.19	0.9964	2.42	1.17	0.7219
LMB	DOC (+P)	5.23	0.53	0.9990	3.66	1.69	0.8072
Bentonite	P	0.37	0.16	0.9946	3.31	9.92	0.8136
Bentonite	DOC	0.49	3.53	0.9994	6.39	3.29	0.7417
DOC-loaded LMB	P	9.09	7.53	0.9998	4.49	5.42	0.6413
P-loaded LMB	DOC	5.22	0.18	0.9977	2.53	1.11	0.6965

C/P molar ratio was still as high as ~32 in the lake water and 48 in the pore water, respectively. Similarly, de Vicente (de Vicente et al., 2008) measured the average DOC concentration in lake water obtained from 31 Danish lakes to be 7.5 mg/L, while Spears et al. (Spears et al., 2016) determined the DOC concentration of 18 lakes across a wide range of lake conditions in Europe and Canada to be 9.95 mg/L, on average. The DOC concentrations of 7.5 and 9.95 mg/L will result in C/P molar ratios of 32 and 42, respectively, assuming that the phosphorus concentration is 0.62 mg/L. Considering that the SRP concentration would be lower than 0.62 mg/L in most cases, the C/P molar ratio would be higher than estimated above. Therefore, understanding the adsorption of phosphate as a function of the DOC concentration (C/P molar ratio) is of great importance. The results in Fig. 2 showed that the phosphate amount absorbed by LMB depended greatly on the DOC concentration (C/P molar ratio). Although DOC did not influence the phosphate uptake significantly at concentrations <2 mg/L, i.e., C/P molar ratios <9 (Duncan multiple comparisons, $p < 0.05$), a further increase in the DOC concentration (C/P molar ratio) caused a linear increase in the residual phosphate concentration after phosphate was adsorbed by LMB (Fig. 2). The residual phosphate concentration continued to increase when the DOC concentration exceeded ~40 mg/L (C/P molar ratio ~167), but the growth rate decreased. This phenomenon can be explained readily by the law of mass action, which states that the rate of a reaction is proportional to the product of the concentrations of the two reactants for a bi-reactant reaction, because the collision frequency increases with increasing concentrations. For the adsorption of phosphate and DOC, the concentration of LMB as a “reactant” is the same, and therefore, at the same phosphate concentration, the higher the DOC concentration, the higher the adsorption amount of DOC via formula (10) and (11) when compared with the phosphate adsorption amount obtained via formulas (6) to (9).

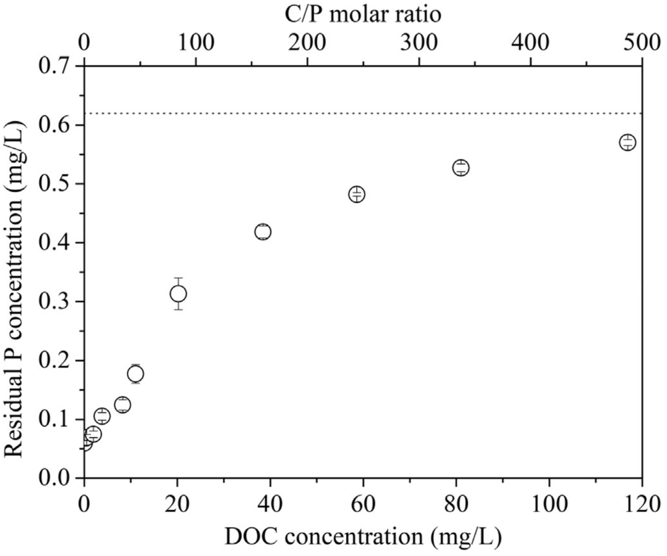

Fig. 2. The performance of LMB to sequester phosphate as a function of the DOC concentration. The top horizontal axis shows the C/P molar ratio calculated from the initial concentrations of phosphate and DOC. The dotted line depicts the initial phosphate concentration. The presented data are the mean values and standard deviations of triplicate experiments.

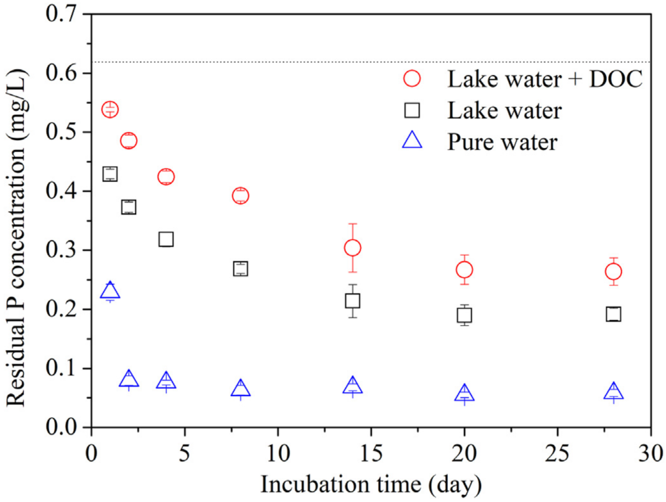

Fig. 3. Capture of SRP from pure water, lake water and DOC-spiked lake water. The dotted line depicts the initial SRP concentration. The presented data are the mean values and standard deviations of triplicate experiments.

The results of the 28-day incubation experiments shown in Fig. 3 further supported the abovementioned conclusion. In pure water, the capture of phosphate by LMB was completed within two days, because there was no statistically significant decrease in the residual phosphate concentration at incubation times longer than two days (Duncan multiple comparisons, $p > 0.05$). The coexistence of soluble components in the lake water, including a DOC concentration of 4.21 mg/L (corresponding to a C/P molar ratio of ~18), greatly reduced the performance of LMB for SRP capture (Fig. 3). However, this decrease cannot be attributed solely to DOC, since a number of other components in the lake water may also influence SRP adsorption, although we believe that DOC played a dominant role based on the results shown in Fig. 2. Similar results on the importance of the DOC concentration in influencing the LMB performance for phosphorus inactivation was recently pointed out by Spears et al. (Spears et al., 2016), who reported that the phosphorus concentrations following LMB applications varied across the lakes and were correlated positively with the dissolved organic carbon concentrations. Spiking DOC by adding humic acid into the lake water to achieve a concentration of 14.21 mg/L further decreased the performance of LMB (Fig. 3), which indicated that an increase in the DOC concentration alone can reduce the sequestration of SRP by LMB. In addition, the existence of DOC not only decreased the adsorption amount of SRP (increased the residual SRP concentration) but also lowered the rate of the SRP adsorption process. The adsorption process occurring in both the lake water and DOC-spiked lake water was much slower than that occurring in the pure water, in which phosphate adsorption reached equilibrium within two days. In fact, a statistically significant decline in the residual SRP concentration continued until day 14, from which time on there was no significant decrease in the residual SRP concentration (Duncan multiple comparisons, $p > 0.05$).

After being applied in lakes, LMB will eventually settled onto lake bed where it can continuously adsorb phosphorus from pore water in sediment, i.e., inactivate phosphorus in lake sediments. The adopted phosphate concentration in this study was 0.62 mg/L, which was representative of phosphorus concentration in pore water of eutrophic lake sediments and was also used in other studies (Dithmer et al., 2016; Lürling et al., 2014; Reitzel et al., 2013). However, this concentration is far higher than that of the water sample taken from the Lake Taihu (Table S1). LMB can scavenge dissolved phosphorus from the water column during the settling process which may takes weeks to months under natural conditions (Spears et al., 2013) or when settled LMB is re-suspended into water column by wind-induced waves and currents. For the inactivation of phosphorus in water column of lakes such as the Lake Taihu, further studies using much lower phosphate concentration may be required. However, the results in laboratory experiments in this study could be really applied for the phosphate binding from water column in heavily eutrophic lakes with relevant high phosphate concentrations. For instance, Lake Dianchi (24°40′–25°02′ N, 102°36′–102°47′ E) is one of the most eutrophicated lakes in China, and high phosphorus concentration in the lake has been reported, reaching 0.4 mg/L in the Caohai section and 0.2 mg/L in the Waihai section (Yan et al., 2019). Similarly, Xie et al. (2013) found that phosphorus concentration reached 0.32 mg/L in the Caohai section and varied from 0.12 to 0.18 mg/L in the Waihai section. Li et al. (2019) collected water samples from the Waihai section for the experiments of phosphorus removal by ferric chloride and determined the initial phosphorus concentration to be 0.19 mg/L.

3.4. Reversibility of the adsorption of phosphate and DOC

To determine whether phosphate or DOC is more strongly adsorbed by LMB, the adsorption isotherm of phosphate on LMB that was previously saturated with DOC and the adsorption isotherm of DOC on LMB that was previously saturated with phosphate were measured, and the results are displayed in Fig. 4. Fig. 4 clearly revealed that, regardless of the presence of DOC on LMB, the phosphate adsorption amount can reach an adsorption amount maximum as high as that of the original LMB (Fig. 4, Table 2). At the same time, phosphate can replace most of the DOC that was previously adsorbed on LMB (Fig. 4). On the other hand, the adsorption of DOC on phosphate-loaded LMB also attained nearly the same adsorption maximum as the original LMB, but DOC displaced little phosphate that was previously adsorbed on LMB (Fig. 4, Table 2). This clearly shows that phosphate is more competitive than DOC for the La sites. Recently, Dithmer et al. (Dithmer et al., 2016) conducted a long-term (400 days) laboratory study, suggesting that the negative effect of DOC on SRP adsorption by LMB is obvious in the short term but probably not permanent, i.e., SRP will eventually be sequestered by LMB. Our results provided solid proof to support that the consideration of Dithmer et al. (Dithmer et al., 2016) is very likely, since the adsorption of DOC is reversible in the presence of phosphate.

However, although phosphate adsorption attained the adsorption maximum, DOC was not totally desorbed (Fig. 4a). Possible reasons are that (i) displaced DOC can be re-adsorbed on the phosphate-loaded LMB due to the high coordination capacity of La; (ii) the O, N or S atoms of DOC interact with the hydroxyl group(s) of the phosphate adsorbed via hydrogen bonding and (iii) DOC interacts with the La sites that were not occupied by phosphate (note that the La/P molar ratio was higher than 1:1, even when phosphate reached saturation, as described in section 3.1). These reasons may also explain why the adsorption of DOC essentially reached its adsorption maximum without the displacement of the phosphate that was previously adsorbed on LMB (Fig. 4b).

To further confirm the reversibility of the adsorption of phosphate or DOC in the presence of DOC or phosphate, the phosphate-saturated LMB or DOC-saturated LMB was desorbed with repeated washing using a DOC solution or phosphate solution. The concentration of either the DOC solution or phosphate solution can assure that the solutes reach their adsorption maxima, provided that DOC or phosphate were present in the water as a single adsorbate. The results shown in Table 3 indicated that both the adsorption of DOC on the phosphate-saturated LMB and the adsorption of phosphate on the DOC-saturated LMB virtually achieved their adsorption maxima by the first washing step, and further washing only resulted in little adsorption. What is the most important is that DOC desorbed little phosphate that was pre-adsorbed on LMB, but most of the DOC pre-loaded on LMB can be displaced by phosphate. Therefore, once the phosphate was adsorbed by LMB, it is stable and will not be released into the water, even in the presence of high DOC concentrations. These results observed in our present study showing that phosphate adsorption is advantageous at low C/P ratios and the adsorbed phosphate is stable in the presence of high DOC concentrations have important implications for phosphorus inactivation in lakes using LMB. That is, LMB can be applied during the season (time) when the C/P ratio in lakes is low, facilitating the adsorption of phosphorus, which will no longer be liberated into water, even after the C/P ratio is increased later. Avoiding the application of LMB when the C/P ratio is high is especially important in soft (low alkalinity) water lakes because of the high La dissolution in soft (low alkalinity) water with high DOC concentration (Reitzel et al., 2017). For instance, the bloom of algae in lakes can not only increase the DOC level via metabolic excretion, which is the autolysis of cells or death from an external factor (e.g., virus attack) in aquatic and artificial ecosystems (Henderson et al., 2008; Hertkorn et al., 2002; Li et al., 2019) but also decrease the SRP concentration by algal uptake (Li et al., 2019). Therefore, the season in which the high chlorophyll *a* concentration would lead to a high C/P ratio should be avoided for LMB application. In addition to the autochthonous material derived from algal or microbiological productivity, allochthonous organic matter from terrestrial inputs also contributes to the DOC in lakes and often dominates the

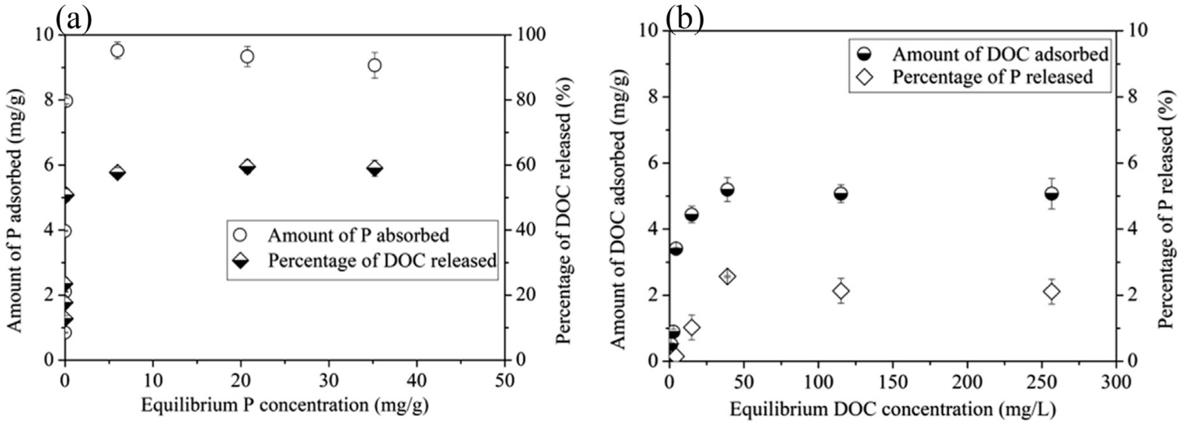

Fig. 4. Stability of the adsorbed phosphate or DOC on LMB. (a). adsorption of phosphate on LMB previously loaded by DOC; (b). adsorption of DOC on LMB previously loaded by phosphate. The presented data are the mean values and standard deviations of triplicate experiments.

Table 3
Results of the desorption of the adsorbed phosphate or DOC by DOC or phosphate, respectively. Presented data are the mean values and standard deviations of triplicate experiments.

Item	Time	Amount adsorbed (mg/g)	Desorption efficiency (%)
Desorption of adsorbed P	1st time	5.48 ± 0.05	1.12 ± 0.65
	2nd time	0.20 ± 0.47	1.49 ± 0.43
	3rd time	0.03 ± 0.49	1.68 ± 0.63
Desorption of adsorbed DOC	1st time	9.78 ± 0.26	58.77 ± 1.54
	2nd time	0.26 ± 0.36	9.47 ± 4.05
	3rd time	0.72 ± 0.40	13.81 ± 1.78

organic carbon balance in most freshwater systems located in temperate climates (Mash et al., 2004; Onstad et al., 2000). Allochthonous organic matter, which is derived from the decomposition of terrestrial plant debris and the humification of soil organic matter, enters aquatic systems mainly from the subsequent runoff of overland water flow during rainfall events (Mash et al., 2004; Onstad et al., 2000). To achieve a good removal efficiency of phosphate by LMB, it would be better to avoid this season. However, because our experimental results revealed that the relative concentration of DOC versus phosphorus determines the efficiency of the phosphorus removal by LMB, it would be important to realize the dynamics of the C/P ratio in a lake rather than the dynamics of the DOC concentration or phosphorus concentration alone prior to the internal phosphorus load management using LMB.

Humic substances such as humic acid and fulvic acid form the major fraction of DOC in aquatic systems, typically compose about 60% of the DOC (Antelo et al., 2007; Stevenson, 1994), and humic acid is thus used as a model DOC in this study and many other studies (e.g., de Vicente et al., 2008; Dithmer et al., 2016; Hiemstra et al., 2013; Lürling et al., 2014). However, DOC consists of a complex mixture of compounds as a result of its variety of sources and continual reworking by photochemical and microbial degradation processes (Scully et al., 2004). As an example, autochthonous and allochthonous DOCs are substantially different. Terrestrial, or allochthonous material, tends to be higher in lignin content with high aromatic content and lower nutrient (N, P) inclusion (Mash et al., 2004). In contrast, autochthonous material derived from algal or microbiological productivity, tends to be more aliphatic with much higher nutrient inclusion (Mash et al., 2004). Therefore, future studies are needed to investigate how these kinds of complex DOC in lakes under environmental concentration affects adsorption of phosphate by LMB.

4. Conclusions

LMB is a widely used phosphorus-inactivating agent in lakes. In our present study, both phosphate and DOC were shown to interact with the La on LMB. The influence of DOC on the phosphate uptake depended greatly on the relative concentration of DOC versus phosphate, which can be expressed as the C/P molar ratio. A significant reduction in the phosphate amount captured by LMB took place at C/P molar ratios exceeding ~9, below which phosphate adsorption was not influenced significantly by DOC. On the other hand, once fixed by LMB, phosphate was essentially not desorbed by DOC, while adsorbed DOC was mostly re-released into water by phosphate. It is presumed that phosphate can interact preferentially with La through stronger binding forces than DOC, but DOC can be adsorbed on LMB, even after it was saturated with phosphate. The results obtained in this study have important implications for the inactivation of phosphorus in lakes using LMB, showing that LMB should be applied in lakes when the C/P molar ratios are low. That is, it is a good strategy to understand the dynamics of the concentration ratio of DOC and phosphate in a lake prior to the use of LMB to achieve a better performance.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2020.115941.

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