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Phosphorus Removal from Eutrophic Waters with a Novel Lanthanum-Modified Diatomite†

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A novel phosphorus adsorbent, lanthanum-modified diatomite was prepared by a simple coating method and exhibited high adsorption and removal efficiency for phosphorus in aqueous solutions. After being modified by lanthanum hydroxide, the surface area of diatomite increased 85-fold and the pore volume increased 390 times. These characteristics are responsible for the increased phosphorus adsorption efficiency. Adsorption behaviour for phosphorus depended mainly on the pH of solution, contact time, initial P concentration and co-exist anion ions. The as-prepared sorbent can be used to remove phosphorus from eutrophic lake water efficiently.

Key Words: Phosphorus, Lanthanum-modified diatomite, Remove, Adsorption, Lake.

INTRODUCTION

Phosphorus, needed for DNA, RNA and energy transfer is the key limiting nutrients in most lake systems[1,2]. Large phosphorus inputs to lakes result in eutrophication and limit the utilization of lake water severely, which are the most extrusive problem of lake in China[3]. Though the external phosphorus input was controlled gradually, the internal phosphorus which releases from lake sediments is becoming the most important source of phosphorus in lake systems[4,5]. The removal of phosphorus by adsorption from water can be an effective method for its recovery and control of eutrophication in lakes and similar confined water bodies[6]. Adsorbents used in the literature are composite adsorbents such as iron oxide[7,8], ferrihydrite-modified diatomite[6], polymer gel[9], TiO_2[10], steel slags[11] modified SiO_2[12], LDH[13] and Fe-Mn binary oxide[14] have been investigated for the removal of phosphorus form an aquatic environment. Although a few studies are available on the use of a support modified with lanthanum as an adsorbent to remove phosphorus from water[15-17], there has been little information on the adsorption of phosphorus by a diatomite modified with lanthanum hydroxide. The objectives of this work are: (1) to characterize the lanthanum modified diatomite by scanning electron microscope (SEM), BET and elemental analysis in detail; (2) to investigate the adsorption of phosphorus on modified diatomite under various common conditions and (3) to study the phosphorus removal efficiency from eutrophic lake water samples by lanthanum modified diatomite.

EXPERIMENTAL

The surface morphology measurements were carried out with a JEOL JSM-6700F scanning electron microscope (SEM). Surface areas were obtained by ASAP2020 M+C system (Micromeritics, USA). The pH measurements were conducted by a PHS-3C pH-meter (Dapu instrumentation Corp. Ltd., Shanghai, China). Diatomite was obtained from Changbai Diatomite Co. Ltd., Jilin, China. $LaCl_3{\cdot}7H_2O$ and KH_2PO_4 (Sinopharm Chemical Reagent Co. Ltd.) are analytical-grade reagents and were used without further purification.

Preparation of lanthanum-modified diatomite: In a typical synthesis, 15 g of diatomite samples were immersed in 100 mL of 6 M sodium hydroxide. The reaction temperature was maintained at 85 ºC for 2 h to partially dissolve Si[6]. The mixture was then placed in 100 mL of 0.2 M $LaCl_3$ under continuous magnetic stirring at room temperature for 24 h. The mixture was centrifuged to remove the supernatant. The solid obtained through centrifugation was washed until no chloride ion could be detected by an aqueous $AgNO_3$ solution and then dried in an oven at 50 ºC, desiccated and stored in polyethylene bottle for future use. The amount of lanthanum hydroxides deposited on the diatomite was determined by dissolving the modified diatomite in 6 M HCl at 40 ºC. Lanthanum ions were determined by the atomic absorption spectroscopy.

Sorption behaviour: 80 mg of lanthanum-modified diatomite was equilibrated with a suitable amount of phosphorus

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solution which the pH was adjusted to desired value with dilute NaOH and HCl in a glass stoppered bottle (100 mL) at 25 ºC under magnetic stirring for a fixed period of time. After recovering the sorbent by centrifugation, the supernatants were analyzed by molybdenum blue method to determine the remaining concentrations of phosphorus in the water samples and the amount of phosphorus adsorbed was calculated using eq. (1).

$$Q_{eq} = \frac{V(C_0 - C_{eq})}{m} \tag{1}$$

Removal of phosphorus from eutrophic lake water: Sorption of phosphorus in Yihai lake water by the lanthanum-modified diatomite was investigated. The lake water samples were first filtered with cellulose acetate filters (0.45 µm) and then spiked with phosphorus to make up two concentrations of phosphorus solution in lake water, *viz.* 10 mg P/L and 5 mg P/L, which represents typical concentration of phosphorus in different source of lake water polluted by domestic wastewaters.

RESULTS AND DISCUSSION

Lanthanum-modified diatomite: The physical parameters of raw diatomite and lanthanum-modified diatomite, such as the BET surface area, total pore volume, average pore diameter and lanthanum content were summarized in Table-1. The BET surface area of lanthanum-modified diatomite is 52.60 m^2/g, which is 82-fold greater than that of raw diatomite. Fig. 1 shows the SEM of raw diatomite and lanthanum modified diatomite. Many pores can be seen on the surface of diatomite (Fig. 1a). The SEM micrograph of lanthanum modified diatomite reveals that raw diatomite frustules are surface modified and the original geometry of the pores is destroyed by the NaOH treatment (Fig. 1b). Initially, colloidal-size lanthanum hydroxide is *in situ* deposited into the macro-pores and larger mesopores of diatomite. After being fully deposited into the pores of diatomite, extra lanthanum hydroxide aggregates on the surface of diatomite particles. The porous structure can still be observed (Fig. 1b), which is beneficial for the phosphorus adsorption.

TABLE-1
PHYSICOCHEMICAL CHARACTERISTIC OF SORBENTS

Property	Raw diatomite	Lanthanum-modified diatomite
BET surface area (m^2/g)	0.64	52.60
Total pore volume (cm^3/g)	0.00079	0.31
Average pore diameter (nm)	49.5	23.8
Lanthanum content (mg/g)	-	126.05

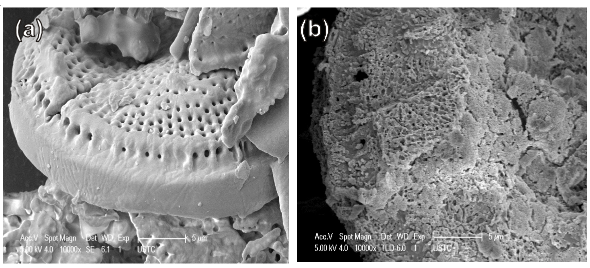

Fig. 1. SEM of raw diatomite (a) and lanthanum modified diatomite (b)

Effect of pH: The anion exchange capacity is strongly governed by the pH of the solution and by the surface chemistry of the solids. The total amount of phosphorus adsorbed by the lanthanum-modified diatomite under different pH values is shown in Fig. 2. The sorption capacity sharply increases with increasing pH from 2 and 4 and then tends to approach a maximum value at pH 5.0, which is maintained until pH 7.0 where after it decreases with further increases in pH. In subsequent phosphorus sorption studies, the pH of the solutions was adjusted to 5.0. Species of phosphate present in lake water include H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} and their relative amounts depend on the pH of the medium. At pH > 7, the predominant species is HPO_4^{2-}, while at pH > 4, the predominant phosphate species is $H_2PO_4^-$, which should have a higher affinity than HPO_4^{2-} for the sorption center.

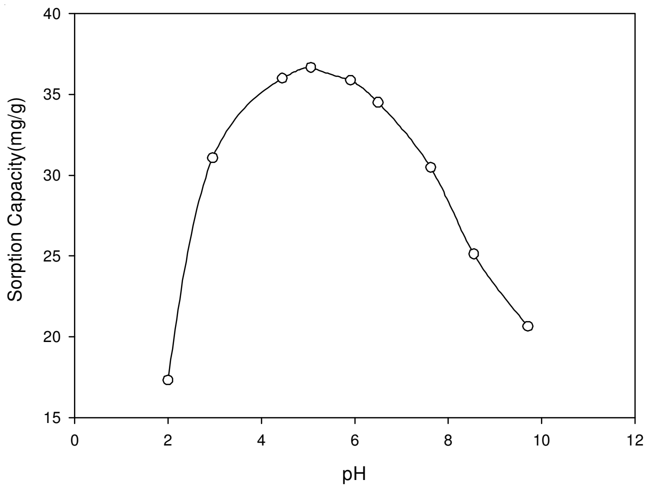

Fig. 2. Effect of pH on phosphorus adsorption

Effect of initial concentration of phosphorus: The effect of initial P concentration in the range of 5 to 50 mg/L on adsorption is shown in Fig. 3. The amount of phosphorus in the solid phase with lower initial concentration of phosphorus was smaller than the amount when higher concentrations were used. It is seen that the adsorption of phosphorus was dependent on the concentration of phosphorus in water samples. The decrease in the initial concentration increased the amount of phosphorus removed. While the percentage phosphorus removal was found to be 98.21 % for 5 mg/L of initial concentration, this value was 56.25 % for that of 50 mg/L.

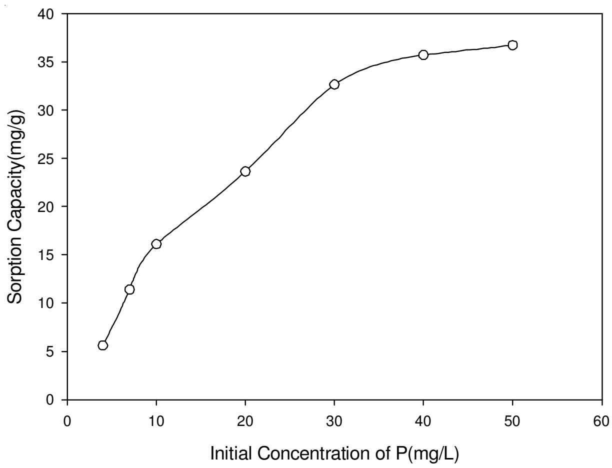

Fig. 3. Effect of initial concentration of phosphorus

Effect of contact time: The effect of contact time on the amount of phosphorus adsorbed was investigated (Fig. 4). The amount of phosphorus adsorbed increased with the increase of contact time and reached equilibrium after 100 min. The equilibrium time is independent of initial phosphorus concentration. But in the first 60 min, the initial rate of adsorption was greater for higher initial phosphorus concentration. The diffusion of phosphate anion ion through solution to the surface of lanthanum-modified diatomite is affected by the phosphorus concentration. An increase of phosphorus concentration accelerates the diffusion of phosphate anion ion from the solution onto modified diatomite due to the increase in driving force of the concentration gradients.

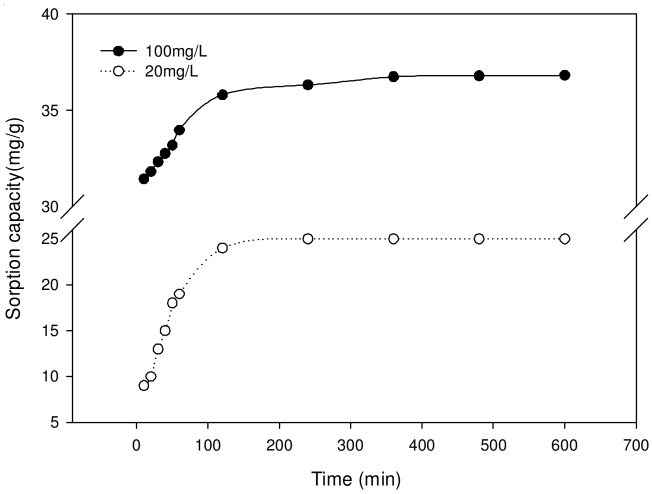

Fig. 4. Effect of contact time

Effect of anions on phosphorus sorption: Anionic species such as chloride, sulphate, oxalate, citrate, acetate, carbonate, nitrate ions are commonly found in lake water and may interfere with the phosphorus sorption process by competing for the sorption sites. To assess the effect of other anions on the sorption efficiency, a 5 mg/L phosphorus solution containing various amounts of other anion ions was used. The tolerance limits of the coexisting ions were defined as the maximum concentration of the foreign substances which could cause an approximately ± 5 % relative error in the sorption capacity determination. The tolerance limit was found to be 1500 mg/L for oxalate and citrate, 2500 mg/L for acetate, chloride and nitrate, 500 mg/L for sulphate and 100 mg/L for carbonate. The results revealed that the lanthanum-modified diatomite is very efficient in removing phosphorus from water samples.

Eutrophic lake water phosphorus removal: The effect of dose of lanthanum-modified diatomite on the amount of phosphorus removal efficiency was studied in spiked lake water (Fig. 5). The equilibrium value of amount adsorbed was observed to decrease with increase in dose. The percentage removal of phosphorus increased with the increase in dose of adsorbent until a plateau is reached. This may be due to the increase in availability of surface active sites resulting from the increased dose of the adsorbent. A lanthanum-modified diatomite dose of 100 mg/L affords a phosphorus removal efficiency of 91 % and 84 % for 5 mg/L and 10mg/L phosphorus respectively. When the adsorbent dose exceeds 140 mg/L, phosphorus removal efficiency is consistently greater than 93 %.

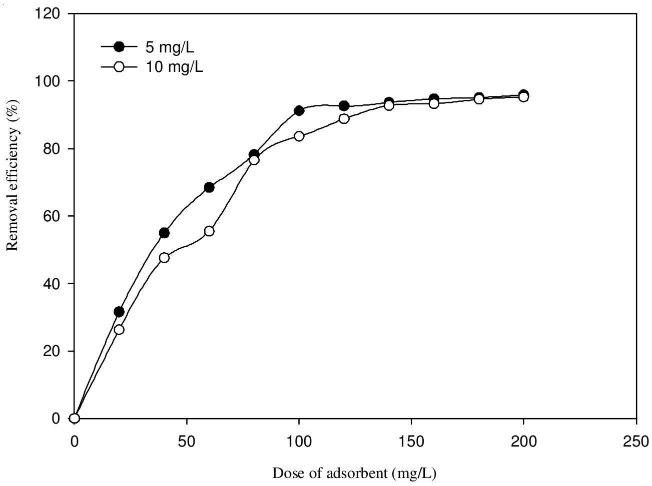

Fig. 5. Effects of lanthanum-modified diatomite dose on removal efficiency of phosphorus in the eutrophic lake water sample

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