



## Research Paper

## Highly-effective phosphate removal from aqueous solutions by calcined nano-porous palygorskite matrix with embedded lanthanum hydroxide



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## ABSTRACT

Efficient phosphate removal from wastewater is critical for the safety of natural water bodies against eutrophication and for the replenishment of unrenewable phosphorus resources. In order to enhance phosphate capture efficiency and exploit raw clay for high value-added products, HPAL-LaOH was fabricated by embedding lanthanum hydroxide onto calcined nano-porous palygorskite clay through a simple-green hydrothermal method where the host palygorskite with cross-linked networks providing abundant binding sites for La(OH)<sub>3</sub> incorporation, allowing the accessibility of phosphate for the adequate crystallization of lanthanum phosphate without triggering pore blockage. Excellent phosphate adsorption capacity (109.63 mg/g) was achieved by HPAL-LaOH, over 13 times higher than that of raw palygorskite, also much higher than commercial pure La(OH)<sub>3</sub> (69.64 mg/g) in batch runs. Interestingly, for solutions below 100 mg/L in a wide pH range of 3–11, almost complete phosphate sequestration (< 0.01 mg/L) was achieved. The presence of high level competing anions (sulfate, nitrate, bicarbonate and chloride) merely exhibited an insignificant effect. Notably, HPAL-LaOH demonstrated satisfactory recyclability, settleability and excellent stability with negligible lanthanum leaching even under ultrasonic challenge. Mechanism analysis revealed that the impregnated La(OH)<sub>3</sub> exerted specific phosphate adsorption where inner-sphere complexation by ligand-exchange played a major role. As compared to several La-based adsorbents developed recently for phosphate sequestration, HPAL-LaOH exhibited great competitiveness in terms of adsorption capacity and La usage. The results indicated the potential utilization of HPAL-LaOH as a highly cost-effective adsorbent for phosphate removal from wastewater.

## 1. Introduction

Excessive phosphorus (P) from drained farmlands, detergents and industrial activities washing into lakes and streams causes eutrophication, which leads to hazardous algae bloom, dissolved oxygen depletion and fish death (Zamparas and Zacharias, 2014), severely disturbing the ecological balance of organisms present in water, and consequently, impairing public health. Thus, feasible techniques are required to suppress P loading into natural aqueous bodies. Adsorption is recommended as a promising option for aqueous pollutant removal due to its simplicity of operation and feasibility of economics (Zhong et al., 2014; Hu et al., 2017; Zhou et al., 2018), which also provides the possibility of P recovery (Loganathan et al., 2014; Mitrogiannis et al., 2017; Zeng et al., 2017; Zhou et al., 2017). To this end, low-cost clay materials have attracted much attention to develop effective adsorbents for enhanced phosphorus removal, including montmorillonite (Tian

et al., 2009), diatomite (Xie et al., 2014a), zeolite (Xie et al., 2014b; Goscianska et al., 2018), aluminum oxide clay (Tanada et al., 2003; Yan et al., 2010), and iron oxide clay (Pan et al., 2009; Acelas et al., 2015), etc. However, their relatively low adsorption capacity and complex preparation procedures play restricting roles on governing the running cost of their utilization in practical wastewater treatment and in-lake eutrophication control (Yin et al., 2016).

Palygorskite, a raw hydrated aluminum-magnesium silicate clay, has been regarded as a promising adsorbent for contaminant removal. The unique structural and adsorptive properties of palygorskite have also been drawn upon for developing aqueous phosphate remover as matrix (Carazo et al., 2018; Yang et al., 2018). Ye et al. (2006) modified palygorskite by hydrochloric acid or thermal treatment and rendered a selective phosphate capture with adsorption capacity of 10.20 mg/g in complex solutions including Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup>. Then, Gan et al. (2009) further activated palygorskite by calcination at 700 °C and

*Abbreviations:* P, phosphorus; La, lanthanum; PAL, raw palygorskite; HPAL, calcined palygorskite at 700 °C for 4 h; HPAL-LaOH, lanthanum hydroxide-impregnated HPAL; HPAL-NaOH, NaOH solution treated HPAL without introducing lanthanum

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the highest phosphate adsorption capacity reached 42.0 mg/g. Unfortunately, using sole raw palygorskite clay for phosphate removal usually present limited active sites and inhomogeneous distribution of inherent components, severely restraining the adsorption efficiency. Thus, developing new generation palygorskite-based cost-effective hybrid adsorbents for enhanced phosphate removal is of much demand.

Attractively, an abundant rare earth element, lanthanum (La), is a promising candidate for the modification of palygorskite due to its excellent affinity with phosphate, along with inexpensive and environmental-friendly nature comparing with Cerium and Scandium. Firsching and Kell (1993) reported the solubility product,  $k_{ps}$ , of lanthanum phosphate as  $10^{-25}$  at 298 K, implying lanthanum phosphate tended to be the most insoluble compound within all the rare earth-phosphate complexes. He et al. (2015) also found lanthanum phosphate was able to form even in solutions with low concentrations and low pH values. However, La particle agglomeration and pore blockage are still major obstacles in the application of current La-based phosphate adsorbents. Notably, Yang et al. (2012) reported host materials with meso/macro-pores and cross-linked framework were ideal candidates for lanthanum incorporation as the macro-porous structure allowed the accessibility of phosphate for the adequate crystallization of lanthanum phosphate without triggering pore blockage. In that case, lots of effort has been put into embedding lanthanum oxide/hydroxide onto synthetic meso/macro-porous polymers, such as polystyrene and carbon nanofiber (Zhang et al., 2012, 2016). Interestingly, palygorskite clay has immanent meso/macro-pores constructed by cross-linked crystalline fibrous networks, providing ideal structure for lanthanum loading without extra structural modification. In addition, compared with those synthetic organic meso/macro-porous materials, the reserves of palygorskite clay are abundant in plenty of regions around the world and the price is extremely cheap (Alvarezayuso and Garcíasánchez, 2003). Moreover, the abundant porosity provided by palygorskite ensure the uniform distribution of lanthanum loaded on the surface and inside the networking pores, avoiding lanthanum particle agglomeration. As accessible functional sites for phosphate are introduced by lanthanum incorporation, the adsorption efficiency of lanthanum palygorskite hybrid adsorbent is expected to be prominent. Thus, a La-based layer coated on palygorskite surface would be a tailor-designed approach for the preparing a novel hybrid adsorbent for P removal.

As few previous studies have reported raw porous palygorskite clay supported lanthanum hydroxide for advanced phosphate removal, this study aims at fabricating a novel palygorskite-based adsorbent HPAL-LaOH with high phosphate adsorption capacity and fast kinetics. The lanthanum hydroxide is expected to exert the dominant specific adsorption to phosphate while the palygorskite plays as a host to provide abundant binding sites for the deposit. It is well known that thermal treatment has a significant effect on the structure of palygorskite, leading to the release of both more calcium and magnesium ions for enhanced phosphate capture and more active groups for the firm combination of the lanthanum hydroxide shell layer and palygorskite core via chemical bonds. Thus, the raw palygorskite was modified by calcination activation before embedding with  $\text{La}(\text{OH})_3$ . Therefore, the objectives of this study include: (1) synthesizing lanthanum hydroxide-impregnated palygorskite (HPAL-LaOH); (2) characterizing the raw palygorskite (PAL), calcined palygorskite (HPAL) and HPAL-LaOH; (3) revealing the phosphate adsorption behavior and mechanism of HPAL-LaOH as a function of solution pH and co-existing ions; (4) evaluating the settleability and stability of HPAL-LaOH after phosphate adsorption.

## 2. Materials and methods

### 2.1. Materials

Raw palygorskite clay was procured from Anbang Minerals Co., Ltd. (Anhui, China), and the < 200 mesh particles were selected for this

**Table 1**  
Chemical composition of the raw palygorskite (wt %).

Constituent	Value (%)
$\text{SiO}_2$	53.897
$\text{Al}_2\text{O}_3$	15.326
$\text{Fe}_2\text{O}_3$	10.905
MgO	8.027
CaO	7.660
$\text{K}_2\text{O}$	2.224
$\text{TiO}_2$	1.961

study. The bulk chemical constitution was revealed in Table 1. The phosphate stock solution was obtained by dissolving analytically pure potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) purchased from Benchmark Chemistry Co. Ltd. (Tianjin, China) in deionized water. Lanthanum nitrate ( $\text{La}(\text{NO}_3)_3$ ), sodium nitrate ( $\text{NaNO}_3$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), sodium chloride ( $\text{NaCl}$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), sodium hydroxide ( $\text{NaOH}$ ), hydrochloric acid ( $\text{HCl}$ ), ascorbic acid and molybdenum acid ammonium were purchased from Guangfu Fine Chemicals Co. Ltd. (Tianjin, China). Lanthanum hydroxide ( $\text{La}(\text{OH})_3$ ) was purchased from Macklin Co. Ltd. (Shanghai, China). All chemical reagents used in this study were analytical grade.

### 2.2. Preparation and characterization of adsorbents

The raw palygorskite (PAL), was calcined in an electric furnace at a range of set temperatures (500 °C, 600 °C, 700 °C, 800 °C and 900 °C) over a series of retention periods (2 h, 3 h, 4 h and 5 h). Among them, the calcined sample with the best phosphate sorption capacity was selected for the following modification and was named as HPAL.  $\text{La}(\text{OH})_3$  suspension was prepared by dropwise addition of 1 mol/L  $\text{NaOH}$  solution into 50 mL 0.1 mol/L  $\text{La}(\text{NO}_3)_3$  solution until pH value reached 10 (Zhang et al., 2012). Afterwards, the suspension was immediately treated with 130 W ultrasonic power for 5 min for sufficient dispersion. Then, 1 g HPAL was added followed by 10 min ultrasonic treatment at 130 W. Subsequently, the mixture was heated at 60 °C for 6 h in a water bath to ensure the loaded La effectively bound to the host. Afterwards, the  $\text{La}(\text{OH})_3$  saturated palygorskite was filtered out and rinsed with deionized water until neutral pH was reached, and then air-dried at 106 °C for 48 h. Finally, the hybrid adsorbent HPAL-LaOH was obtained. For comparison, a sample without introducing La (denoted HPAL-NaOH) was prepared using the similar procedures, but in the absence of  $\text{La}(\text{NO}_3)_3$ , where the HPAL was only treated in  $\text{NaOH}$  aqueous solution.

Surface morphologies of the adsorbents were analyzed using a field emission scanning electron microscope (FESEM, Quanta FEG 250, USA). Crystalline phases were characterized by employing X-ray diffraction (XRD, Rigaku D/MAX-2000, Japan) using a monochromator with the irradiation source of  $\text{Cu K}\alpha$  (40 kV, 25 mA) and wavelength of 1.54060. The scanning range and step were 10–80° and 0.02°, respectively. Fourier transformation infrared spectrometer (FT-IR, Perkin Elmer, USA) was employed to detect the specific functional groups of adsorbents by using dry potassium bromide for background subtraction. The nitrogen  $\text{N}_2$  adsorption-desorption test was conducted at liquid nitrogen temperature using a gas adsorption analyzer (ASAP 2020M, Micromeritics, USA), and then the specific surface area and average pore diameter were analyzed accordingly. The interactions between HPAL-LaOH and phosphate were probed from X-ray photoelectron spectroscopy (XPS, PHI 5700 ESCA System, USA) using a monochromatic rotating anode Al  $\text{K}\alpha$  excitation source with pass energy of 30 eV. The La content of HPAL-LaOH was measured by X-ray fluorescence spectrometer (XRF, PW4400, Netherland).

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