



Robust phosphate capture over inorganic adsorbents derived from lanthanum metal organic frameworks

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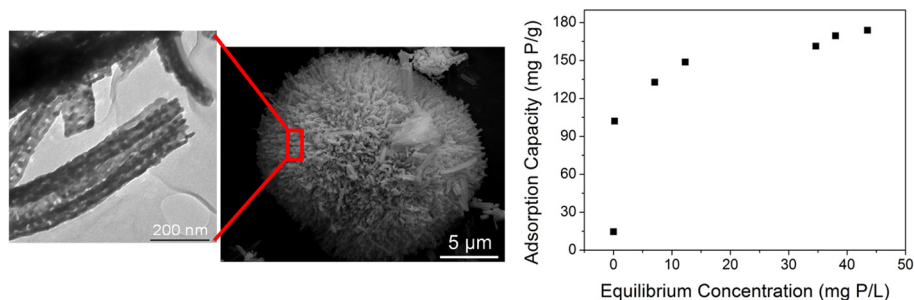
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HIGHLIGHTS

- A superior phosphate scavenger was designed deriving from La-MOF.
- The adsorbent has a hierarchical structure of microsphere-nanorod-nanoparticle.
- A high adsorption capacity and a high P/La ratio were obtained concurrently.
- The adsorbent exhibits a much higher adsorption capacity of over 170 mg P/g.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 13 April 2017

Received in revised form 9 June 2017

Accepted 10 June 2017

Available online 12 June 2017

Keywords:

Adsorption

Phosphate removal

Water treatment

Metal organic framework derivative

Lanthanum containing adsorbent

ABSTRACT

Excessive phosphate in water can cause severe water quality problems owing to its somatotropic effect on microorganisms. Herein, a superstructural phosphate scavenger, La-MOF-500, composed of $\text{La}_2\text{O}_2\text{CO}_3$, is rationally designed by derivation from lanthanum metal organic frameworks ($\text{La}(1,3,5\text{-BTC})(\text{H}_2\text{O})_6$) by calcination. La-MOF-500 has a hierarchical micro/nano structure of microsphere-nanorod-nanoparticle: urchin-like microsphere is comprised of many nanorods and the individual nanorod was formed by piling up plentiful thin nanoparticles. The hierarchical micro/nano structure provides La-MOF-500 with an intriguing phosphate capture capacity of 173.8 mg P/g and a high utilization of lanthanum active sites, simultaneously, which was a challenge in previous research. Moreover, La-MOF-500 exhibits a good tolerance of foreign species. Even in the water from Songhua River (China), La-MOF-500 can remove phosphate to be less than 10 $\mu\text{g P/L}$. This development is expected to be meaningful for practical water purification.

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1. Introduction

Phosphorus, a building block for nucleic acids, proteins and energy carriers, is an essential element for the growth of all organisms [1]. The excessive intake of phosphorus in water bodies is mainly caused by the increasing discharge of domestic, industrial or agricultural wastewater containing phosphorus. Pol-

lution caused by excessive phosphorus can spur abnormal growth of algae, bacterial and aquatic plants, and thus renders surface water eutrophication as well as endangers bio-stability of drinking water [2–5]. It is of specially importance to remove phosphate from water, since it is widely accepted that phosphate is the only form of phosphorus that can be directly assimilated by organisms [6,7]. By far, various attempts have been made to remove phosphate from water in recent years, therein the preferred routes have applied the adsorption-based process due to simplicity, low energy consumption, high efficiency and fast removal rate [2,8–12].

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Recently, the stronger bond of lanthanum (La) species to phosphate (solubility product of lanthanum phosphate $pK = 26.16$) than other adsorbents highlight the application in removing excess phosphate in the human body and in water [13–21]. Lanthanum is an abundant and inexpensive rare earth element and considered to be environmental benign together with ace biocompatibility [19,22,23]. It exhibits superior adsorption properties, high efficiency towards low concentration targets and outstanding selectivity [17,18,24]. One well-known and extensively used material based on La for lake restoration is Phoslock, which is a commercial product developed by CISRO [25]. However, lanthanum active species conventionally need to be loaded in/on some supports to maintain high dispersion and a high usage efficiency of lanthanum active sites (P/La ratio), which will sacrifice the adsorption capacity of the whole adsorbents as a price [24,26–29]. Contrarily, if a higher adsorption capacity was the goal, the usage efficiency of lanthanum active sites would be limited obviously. Thus, it is a challenge but an aspiration to design a La-based phosphate scavenger with both high adsorption capacity and high P/La ratio.

Metal–organic frameworks (MOFs) as a new class of crystalline 3-dimensional materials, are formed by complexation between ligands and metallic centers [30–32]. Given their unique properties of tunable structures, huge porosity and pore geometry [31,33–35], MOFs have been used for the aqueous-phase adsorption of different pollutants in water [36–40]. Nevertheless, to our best knowledge, few studies have been conducted to investigate the removal of phosphate from water by lanthanum MOFs or even MOFs via the adsorption [41,42]. It is because that original MOFs may be not that suitable for phosphate adsorption. For MOF materials, the combining of phosphate should mainly happen at metal sites achieved by complex reaction. But many metal sites in the MOFs indeed were occupied in advance by organic bridging linkers also by complex reaction. Therefore, if the combining ability of metal sites with phosphate is much higher than organic bridging linkers, the adsorption capacity would be high, but the toxic organic bridging linkers might be released into water during adsorption. If the combining ability of metal sites with phosphate is lower than or comparable to the organic bridging linkers, the adsorption capacity would be modest.

Thus, in order to obtain high performance phosphate adsorbents, we firstly constructed a La containing hierarchical structure by formation of La-MOF. And then by derivation from La-MOF via calcination, we rationally prepared an urchin-like phosphate scavenger (La-MOF-500), wholly composed of $\text{La}_2\text{O}_2\text{CO}_3$ active nanorods. At a deeper level, the $\text{La}_2\text{O}_2\text{CO}_3$ nanorod individual is not solid but formed through the agglomeration of numerous thin nanoparticles. This superstructure could provide more reactive sites to bind with phosphate, and as a result exhibited a robust phosphate capture capacity of 173.8 mg P/g at room temperature, which was several times higher than the values reported for previous phosphate La-adsorbents. Simultaneously, the products presented a high utilization of La sites (a high P/La ratio of 1.04). Additionally, La-MOF-500 could reduce low phosphate concentration to be less than 10 $\mu\text{g P/L}$, whether the water was synthetic or from Songhua River (China). This development is expected to be meaningful for practical water purification. This is the first work on the development of phosphate adsorbents based on MOFs derived pure inorganic materials. It is meaningful to design high performance phosphate adsorbents.

2. Experimental

2.1. Materials

Lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) was provided by Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). 1,3,5-

benzentricarboxylate (1,3,5-BTC or H_3BTC) was purchased from Hans Chemical Reagent Co., Ltd. (Beijing, China). Sodium hydroxide (NaOH) and potassium dihydrogen phosphate (KH_2PO_4) were purchased from Xilong Chemical Co., Ltd. (Guangdong, China). All of the chemical reagents used were analytical grade and used as received without further purification.

2.2. Fabrication of La-MOF

The construction of La-MOF was achieved by the complex reaction between La^{3+} and ligand in room temperature. First, 10.825 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was mixed with water to obtain a 500 mL solution. Then 500 mL of ligand solution was prepared by dissolution of 5.2535 g H_3BTC in water/ethanol mixture (v/v, 1:1). The same volume of the above two solution were mixed together at 25 °C, and the reaction was operated under a 135 r/min for 1.5 h. After 0.5 h settling, the as-prepared products were rinsed with water/ethanol mixture (v/v, 1:1) for 5 times and then dried in an oven at 60 °C. The above fabrication can be scaled up.

2.3. Fabrication of MOF derived adsorbents

The thermal pyrolysis of La-MOF precursor was carried on by heating the sample to target temperature at a rate of 10 °C per minute in a furnace in air. The peak temperature was maintained in range of 400 °C to 800 °C for 3 h and then cooled down to room temperature naturally. The corresponding samples were named as La-MOF-400, La-MOF-500, La-MOF-600, La-MOF-700 and La-MOF-800, respectively.

2.4. Characterization

FT-IR spectra of the samples were recorded on a PerkinElmer Spectrum One B spectrometer with KBr as the reference. The crystal structure of the samples was investigated using an X-ray diffraction (XRD) by Bruker D8 Advance diffractometer using Cu KR radiation as X-ray source. The microstructures of the products were observed on a Helios Nanolab600i field emission scanning electron microscope (FE-SEM). Transmission electron microscope (TEM) imaging analysis was performed with JEM1400 (JEOL, Japan). Thermal analyses (TGA) data were obtained on a STA449C (NETZSCH) instrument at a heating rate of 10 °C/min. The Brunauer–Emmett–Teller (BET) surface area and porous structures were analysed based on N_2 adsorption–desorption isotherms by using an ASAP 2020 M (Micromeritics Instrument Corp., USA).

2.5. Phosphate adsorption experiments

A series of batch tests were conducted to investigate the phosphate adsorption performances of our prepared adsorbents. The phosphate solutions in studies were prepared with KH_2PO_4 and DI water. All solution samples were filtered through a 0.45 μm membrane syringe filter prior to analysis. The filtrate for phosphate concentration was analyzed by Mo-Sb anti-spectrophotometer method using UV-vis spectrophotometer (HACH, DR5000, America). But when the initial phosphate concentration was lower than 1 mg P/L, the phosphate concentration was determined by inductively coupled plasma mass spectrometry (ICP-MS, 7700 Series, Agilent Technologies, US).

The effect of calcination temperature on the phosphate adsorption capacity of the adsorbents was investigated to choose an optimal adsorbent. The investigated adsorbents were La-MOF-400, La-MOF-500, La-MOF-600, La-MOF-700 and La-MOF-800, respectively. 0.8 g/L of adsorbent was added into 50 mg P/L solution and then shaken at 25 °C for 12 h at 150 rpm.

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