



Enhanced adsorption of phosphate by flower-like mesoporous silica spheres loaded with lanthanum



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ABSTRACT

Monodispersed flower-like mesoporous silica spheres doped with lanthanum were synthesized *via* a facile method and explored as novel adsorbents for efficient phosphate adsorption for the first time. The synthesized adsorbents possessed a flower-like structure, especially with unique mesoporous channels featuring with small inner pores and wide outer pores. By raising lanthanum loading, the surface areas and pore volumes of resulting adsorbents were observed to continuously decrease, accompanied with gradually increasing pore sizes; that led to a dramatic improvement in phosphate adsorption from water. By taking cost effectiveness for practical application into consideration, the adsorbent with a theoretical La/Si molar ratio of 0.1 possessed a promising performance as compared to the literature ever reported, thanks to the large outer mesopores likely minimizing the diffusion problem caused by the pore blocking when LaPO₄ nanorods formed during adsorption. In the kinetic study, its phosphate adsorption followed the pseudo-second-order equation better, suggesting chemisorption. Meanwhile, superior phosphate adsorption capacities were achieved within the pH range of 3.0 and 6.0; and almost unaffected by the presence of F⁻, Cl⁻, NO₃³⁻, and SO₄²⁻.

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1. Introduction

Excessive presence of phosphorous in water bodies is one of the major causes to eutrophication, which leads to the outbreaks of algal bloom, diminishes dissolved oxygen, lowers water quality, and reduces biodiversity in aquatic ecosystems [1,2]. Therefore, it is of vital importance to reduce and control the level of phosphorous in the industrial, urban, and agricultural wastewater prior to its discharge into environment. In this regard, several methods, including chemical precipitation, biological treatment, ion exchange and adsorption, have been investigated to remove phosphorous from aqueous solution [3]. In particular, the adsorption-based process is considered as one of the promising routes, due to its simple operation and low sludge production [4,5]. Until now, various types of new adsorbents have been developed for phosphorus removal; especially the composites made from metal oxide or hydroxide depositing on the surface of porous support materials, among which activated carbon and silica are

popular options due to their non-toxic nature [6–8]. In general, commercial activated carbon is consisting of disordered porous structure and irregular pore size distribution. The portions of micropores, mesopores, and macropores in activated carbon are varied largely depending on the raw materials used during synthesis. Fundamentally, the richness of micropores endows a potential for large surface area of activated carbon, but lowering mass transfer and in turn adsorption capacity/rate. By contrast, mesoporous silica has received considerable attention owing to its attractively unique features, such as a highly ordered structure, ultrahigh surface area, tunable pore size and structure, as well as favourable surface chemical property for functionalization or modification [9,10].

Recently, there has been a significant progress made in developing metal-modified mesoporous silica materials as phosphate adsorbents [11–18]. Until now, a variety of metals, including Fe, Al, Zr and La, have been successfully impregnated into mesoporous silica, such as SBA-15 or MCM-41, to form novel adsorbents with tailorable properties [8,11–18]. In particular, mesoporous silica materials incorporated with lanthanum (La) have exhibited several promising advantages in phosphorus adsorption, *i.e.* a superior adsorption capacity, wide operating pH range, and high removal rate in low phosphate concentration [13,17–20]. Since metal oxides

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which are embedded into mesoporous silica act as active sites specifically adsorbing phosphate, high loadings of metal oxides are usually desirable to enhance adsorption capacity. Nevertheless, excessive loading of metals might attack and partially destruct the ordered porous framework, resulting in a less access to the adsorption sites inside the ruined pores and in turn a lower adsorption capacity [11,16,21,22]. For example, Shin et al. reported that SBA-15 modified with a high loading of Al (30%) exhibited lower phosphate adsorption capacity (19.2 mg P/g) than those of 10% (26.7 mg P/g). This was attributed to that the pore structure was destructed so that adsorbates could not access the adsorption sites inside the blocked pores [16]. In Yang's work by using SBA-15 with relatively large pores of 8.87 nm, the high loading of La in the silica materials lowered La usage efficiency [18]. This was possibly explained by the heterogeneous nucleation and subsequent growth of LaPO₄ nanorods during adsorption; which blocked the confined channels and caused the diffusivity problem [18].

In 2011, Gai et al. reported the synthesis of a family of novel flower-like mesoporous silica (FMS) spheres for drug delivery; which exhibited unique fine pore systems with narrow inner channels and wide outer pore openings, offering an easy and high accessibility to a large number of active sites inside the pores [23,24]. They are shown as promising supporting material candidates, potentially leading to the formation of superior phosphate adsorbents with improved diffusion characteristic and adsorption performance, as compared with the traditional mesoporous silica, e.g. SBA-15 or MCM-41.

Herein, we designed novel phosphate adsorbents by modifying FMS with lanthanum; to the best of our knowledge, this was reported for the first time. The structural and morphological properties of synthesized La-modified FMS, as well as their corresponding phosphate adsorption behaviours were investigated in detail. In particular, the sample FMS-0.1La (theoretical La/Si molar ratio = 0.1) exhibited the highest phosphate removal efficiency in terms of P/La molar ratio; thereby was selected for study on its phosphate capture by varying time, pH and co-existing ions. Our study suggests the developed flower-like mesoporous silica spheres loaded with La be a good choice for the adsorption of phosphate from aqueous environment.

2. Experimental

2.1. Chemicals and materials

All of the chemicals were used as received without further purification. Cyclohexane (≥99%), 1-pentanol (≥99%), cetyltrimethylammonium bromide (CTAB), and tetraethyl orthosilicate (TEOS, 98%) were purchased from Sigma–Aldrich. Lanthanum nitrate hexahydrate [La(NO₃)₃·6H₂O] was purchased from Fluka. Potassium dihydrogen phosphate (KH₂PO₄), urea, acetone, NaCl, NaSO₄, NaNO₃, NaF, and Na₂CO₃ were the products from Merck Pty Limited, Australia. Other chemicals were obtained from Biolab Ltd, Australia.

2.2. Synthesis and characterization of adsorbents

The flower-like mesoporous silica (FMS) spheres were synthesized as reported [23,24]. Typically, 1.5 mL of pentanol was dissolved in 30 mL of cyclohexane, followed by adding 2.7 mL (12 mmol) of TEOS to form solution A. 1.87 g (5.14 mmol) of CTAB and 0.6 g of urea were dissolved into 30 mL deionized (DI) water to get solution B. Subsequently, solution B was quickly added into solution A under vigorous stirring. After 30 min, the mixture was transferred into a Teflon-lined autoclave, which was then heated at 120 °C for 4 h. The obtained product was washed with acetone and deionized (DI) water, and dried in oven. The final product was calcined in air from 25 °C to 550 °C (1 °C min⁻¹), after which the calcination was maintained at 550 °C for 6 h.

The modification of FMS with lanthanum oxide was carried out as following: La(NO₃)₃·6H₂O was selected as the lanthanum precursor and incorporated into FMS using the ethanol evaporation method [18,19]. Typically, 0.4 g of FMS was added into 100 mL of ethanol solution containing desired amount of lanthanum precursor. The mixture was stirred at 60 °C for 24 h, and then the temperature was increased to 80 °C to evaporate the ethanol completely. The product was calcined at 550 °C for 5 h. The theoretical molar ratios of La versus Si were varied from 0.02, 0.04, 0.1, to 0.2. In this way, four samples with different theoretical La/Si molar ratios were obtained and denoted as FMS-xLa, e.g. FMS-0.02La, FMS-0.04La, FMS-0.1La and FMS-0.2La, respectively. The parent sample was prepared and referred as FMS for comparison.

Surface morphologies of the samples were examined by scanning electron microscopy (SEM, JSM-7401F, JEOL Ltd., Japan) and energy dispersive spectroscopy (EDS, Horiba EX-250, Japan). Transmission electron microscopy (TEM, JEM2010-HR, Japan) was used to characterize the sample at an accelerating voltage of 200 kV; in which the sample was firstly dispersed in ethanol *via* ultrasonic treatment and then collected with a carbon copper grid. X-ray powder diffraction (XRD) patterns were recorded in the 2θ range of 5–80° with a scan speed of 1°/min by using a diffractometer (Bruker D8 Advance diffractometer, Germany) with Cu Kα radiation (40 mA, 45 kV). Nitrogen adsorption–desorption isotherms were measured at 77 K using ASAP 2010 (Micromeritics Inc., USA). Prior to analysis, the samples were degassed at 120 °C for 12 h under vacuum. The specific surface area, S_{BET}, was determined from the linear part of the BET plot (P/P₀ = 0.05–0.20). The pore size was calculated from the desorption branch of isotherm by using Barrett–Joyner–Hallenda (BJH). The total pore volume, V_{total}, was evaluated from the adsorbed nitrogen amount at a relative pressure of 0.98.

2.3. Phosphate adsorption experiments

A series of batch tests were conducted to investigate the phosphate adsorption performances of the adsorbents. The solution of different phosphate concentrations was prepared by dissolving desired amount of KH₂PO₄ in DI water. The phosphate concentration was analysed by Autoanalyzer 3 (Bran and Luebbe Inc., Germany).

In equilibrium experiments, 0.025 g of the adsorbent was added into 50.0 mL of phosphate solution with various initial concentrations in polypropylene bottles. The pH of the solution was adjusted to 5.0 by 0.10 M HCl or 0.10 M NaOH. The samples were placed in the shaker bath at 25 °C for 48 h. The phosphate concentration was analysed after centrifugation for 10 min at 12,000 rpm. The amount of phosphate adsorbed onto the sample at the equilibrium (q_e) was calculated by Eq. (1),

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

where C₀ and C_e are the initial and equilibrium phosphate concentrations in solution (mg P/L), respectively; V is the volume of solution (L) and m is the mass of adsorbent (g).

The equilibrium data were fitted to the Langmuir and Freundlich isotherm models, and their equations were shown as Eqs. (2) and (3) [25,26], respectively,

$$\text{Langmuir model: } q_e = q_m K_L \frac{C_e}{1 + K_L C_e} \quad (2)$$

$$\text{Freundlich model: } q_e = K_F C_e^{1/n} \quad (3)$$

where q_m (mg P/g) is the amount of adsorption in Langmuir adsorption model corresponding to the maximum adsorption

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