Phosphate adsorption on lanthanum hydroxide-doped activated carbon fiber

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ABSTRACT

A novel adsorbent, lanthanum hydroxide-doped activated carbon fiber (ACF-LaOH), has been prepared by the ultrasound-assisted chemical precipitation method for phosphate removal from waste water. Based on the single-factor method, response surface methodology (RSM) by using a Box–Behnken design (BBD) was applied to assess the mutual interactions and effects between the three factors and the optimized preparation conditions (concentration of La^{3+} of 0.11 mol/L, ultrasonic power at 206 W and ultrasonic time of 7.3 min). Adsorption kinetics and isothermal adsorption studies showed that the pseudo second-order model and the Langmuir isotherm fitted the experimental data quite well, indicating that the adsorption process was mainly through chemical interactions. At last whereas most importantly, the phosphate adsorption mechanism was investigated by analyzing the scanning electron microscopy (SEM), fourier transform infrared (FT-IR) spectroscopy and the relationship between the adsorption amount and the pH of phosphate solution. The results demonstrated that ligands exchange, electrostatic interactions and Lewis acid–base interaction were the three main mechanisms for phosphate adsorption. The ligands exchange and electrostatic interactions became weaker, but the Lewis acid–base interaction was strengthened with the increase of pH values giving rise to the decrease of adsorption amount.

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1. Introduction

Excess phosphorus in water body may cause eutrophication and significant environmental problems to water resources [1,2]. Reducing or removing the phosphate in wastewater is one of the most important tasks for abbreviating the pollution of water bodies. Various techniques have been applied for phosphate removal successfully, such as chemical precipitation, adsorption and biological process. However, biological process is unsteady because the quality of water plays a great impact on phosphate removal ratio. Meanwhile, chemical precipitation often consumes a large amount of flocculant and coagulant accompanied by sludge treatment and disposal problems [3]. Adsorption is an alternative and promising phosphate removal method, especially for wastewater with low phosphate concentration [1], wherein development of high-quality phosphate adsorbents is the key.

In the last decade, many endeavors to the exploration of phosphate adsorbents have successfully led to aluminum hydroxide and aluminum oxides [4,5], iron and iron oxides [6], layered double hydroxides [7], mesoporous silicates [8], natural minerals [9], solid wastes [10]. In particular, lanthanum has attracted special attention for its high phosphate adsorption capability, nontoxic and environmental friendliness [11]. The lanthanum doped with suitable substrates has proved to be ideal for improving phosphate adsorption efficiency [11–14]. In our previous study [15], lanthanum oxide-doped activated carbon fiber (ACF-LaO) has been successfully synthesized by a typical method comprising immersion–filter–drying–baking–screening and other steps. The activated carbon fiber, which has a low phosphate adsorption amount (about 0.6 mg/g) from our previous experiment, serves as support materials due to its large specific surface area, cheap and easy availability. It has been verified that ACF-LaO functions as an excellent phosphate adsorbent by virtue of good chemical stability, excellent physical strength.

In our latest study [16], aion-ligand exchange was suggested to be the most important mechanism for phosphate adsorption onto ACF-LaO, by producing hydroxyl groups on lanthanum oxide which provides coordination sites for phosphate to bind onto La (III). Some studies have reported that metal hydroxide shows a stronger capacity for ion exchange [7,17,18]. Accordingly, lanthanum hydroxide ($La(OH)_3$) may provide more adsorption sites than lanthanum oxide. Thus, efficient synthesis of $La(OH)_3$ doped ACF is of great demand.

To this end, we prepared ACF-LaOH by ultrasonic-assisted chemical precipitation. With the action of ultrasonic cavitation, the generation of a transient high-temperature, high-pressure

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environment in the solution leads to strong shearing and fragmentation into particles, disrupting the aggregation between particles and controlling the size and size distribution. Meanwhile, the shock-wave that arisen by the transmission of ultrasound in liquid phase should facilitate the La(OH)$_3$ particles into the framework of ACF for efficiently load of La(OH)$_3$ [19,20]. The objectives of this study are to: (1) optimize the preparation conditions of ultrasonic precipitation method using response surface methodology (RSM); (2) verify the adsorption performance of ACF-LaOH; (3) reveal the different mechanisms of phosphate adsorption onto ACF-LaOH. Results of this research demonstrated that ACF-LaOH were more effective in phosphate removal than ACF-LaO.

2. Materials and methods

2.1. Materials

ACF was procured from Qinhuangdao Zichuan Carbon Fiber Co., Ltd. (China), and according to the supplier's report, the specific surface and mean pore size is $1326 \, m^2 \, g^{-1}$ and 1.8 nm, respectively. Potassium dihydrogen phosphate, lanthanum nitrate, sodium hydroxide, ascorbic acid and molybdenum acid ammonium were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All the chemical reagents used were of analytical grade.

2.2. Preparation and characterization of adsorbents

Pretreatment of ACF: ACF was fully washed for several times with deionized water and sheared to desired size fragment (0.4–0.6 cm). A 1 mol/L of NaOH solution was added into 5 mL of different lanthanum nitrate solution in 100 mL beakers for pH adjustment to 10.0. The resulting mixtures were then treated by ultrasonic for 2 min immediately resulted in La(OH)$_3$ suspension. 0.100 g of ACF was added into the La(OH)$_3$ suspension, which was treated by ultrasonic with specific power and time. The solid was collected by filtration, washed with deionized water, and then dried at 105 °C.

Surface morphologies of ACF-LaOH were observed with scanning electron microscopy (SEM) using a JSM-6700 F instrument (JEOL Co., Ltd., Japan). Fourier transform infrared (FT-IR) measurements were performed on a Nicolet FT-IR 380 instrument (Thermo Scientific Co., Ltd., USA). The spectrum of dry potassium bromide was taken for background subtraction. Each spectrum was obtained by accumulating 152 scans in transmission.

2.3. RSM experimental design

Box–Behnken experimental design, which is a widely used form of RSM [21], was applied for the optimization of ACF-LaOH preparation, using the design expert statistical software (version 7.1.6, STAT-EASE Inc., Minneapolis, MN, USA). According to the method of Box–Behnken design experiment, concentration of La^{3+} (X_1, mol/L), ultrasonic time (X_2, min), and ultrasonic power (X_3, W), which had a great effect on the removal rate of phosphate, were selected as design variables. The validity of the model was expressed in terms of the coefficient of determination R^2, and the adequacy of the model was further evaluated by analysis of variance (ANOVA). Please see more information about RSM experimental design in supporting material (Section S1, Supplementary Material).

2.4. Phosphate adsorption experiments and analytical methods

The phosphate solutions of various concentrations were obtained by dissolving potassium dihydrogen phosphate (KH$_2$PO$_4$) in deionized water. Adsorption processes for single factor experiments were conducted as follows: 0.100 g of adsorbent was added

into 50 mL conical flask filled with 40 mL (2.5 g/L dosage) of phosphate solution (30 mg/L). The sealed flasks were then placed in a thermostatic shaker bath at room temperature for 4 h, and shaken at 120 rpm. At the end of adsorption process, the solution was filtered through a 0.45 μm membrane syringe filter and analyzed for adsorption efficiency.

As for the equilibrium experiments, the same experimental procedure was performed as aforementioned procedures by phosphate adsorption for 6 h in various initial concentrations (10–70 mg/L). The removal efficiency (E, %) and adsorption capability (Q_e, mg/g) of phosphate on ACF-LaOH were calculated by Eq. (S3, S4) (see Section S2, Supplementary Material). All experiments were conducted for three times, and the mean values of the results were given throughout this paper to reduce the experimental errors.

Adsorption kinetic experiments were conducted as follows: 0.300 g of adsorbent was added in 300 mL phosphate solutions with various initial concentrations (10, 20, 30 mg/L, respectively). A 2 mL of solution was taken out of the flask at given time intervals for the analysis of phosphate concentrations after filtration.

To investigate the influence of pH on phosphate adsorption, ACF-LaOH (1.00 g/L) was added into a 30 mg/L of phosphate solution adjusted with 1 mol/L of NaOH and HCl solutions to give various initial pH values (2.0–12.0). The change of pH values of an independent adsorption process was also studied: flasks charged with 30 mg/L of phosphate solutions, and 2.50 g/L of dosage of adsorbent were used as a standard approach to remove phosphate at various times.

The concentrations of the phosphate solutions were determined by using the ascorbic acid method [22]. The absorbance of the solutions was analyzed by 721 spectrophotometer (Shanghai Metash Instruments Co., Ltd., China). The pH of the solution was determined by Sartorius PB 220 pH meter (Sartorius, Germany).

2.5. Stability of ACF-LaOH

The amount of lanthanum in the ACF-LaOH was investigated before and after the addition of adsorbent in the phosphate solutions at 30 mg/L. The concentration of residual lanthanum ions after adsorption process can therefore be determined. The material was burned at 600 °C in an oven, and the residue was dissolved with a 1 mol/L of sulfuric acid solution. The solution was collected in a proper sample tube using a syringe and filtered with a filter disk with a pore size of 0.45 μm. At the end of the adsorption process, the solid was treated using the same procedure mentioned above after being dried. The residual solution was collected after filtration. The concentration of lanthanum in the filtrate was analyzed by using an inductively coupled plasma atomic emission spectrometer (ICP) (Shimadzu SEQUE-NTIAL PLASMA SPETROMETERICPS-1000II).

3. Results and discussion

3.1. The effect of different factors on phosphate adsorption

Influence of each factor on phosphate removal by ACF-LaOH is investigated by the single-factor method. The experimental results are shown in Fig. 1. The effect of La^{3+} concentration on the removal efficiency is shown in Fig. 1a. The phosphate removal first increases and then decreases with the increase of La^{3+} concentration from 0.01 to 0.13 mol/L. This may be due to the fact that the solution become viscous in which particles is easy to generate the agglomerate state at high concentrations, the large-size particles would in turn obstruct the loading of La(OH)$_3$ and reduce the adsorption sites on the surface of ACF.

It is observed that in Fig. 1b that the phosphate removal efficiency first increases sharply, and then keeps mostly steady with an