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Phosphate adsorption on aluminum-coordinated functionalized macroporous–mesoporous silica: Surface structure and adsorption behavior

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ABSTRACT

In this study, Al(III)-coordinated diamino-functionalized macroporous–mesoporous silica was synthesized and characterized by X-ray diffraction, N_2 adsorption–desorption, Fourier transform infrared spectroscopy, scanning and transmission electron microscopy. Because of well-defined and interconnecting macroporous–mesoporous networks, the resulting adsorbent (MM-SBA) exhibited a significantly better phosphate adsorption performance and faster removal rate, as compared with the mesoporous adsorbent (M-SBA). Based on the Freundlich and Langmuir models, the phosphate adsorption capacity and the maximum adsorption capacity of MM-SBA were 7.99 mg P/g and 23.59 mg P/g, respectively. In the kinetic study of MM-SBA, over 95% of its final adsorption capacity reached in the first 1 min; whereas that of M-SBA was less than 79%.

1. Introduction

Phosphorus is an important nutrient for living species, which is typically present at a low concentration in environment serving as the limiting factor for aquatic plant growth. To date, the increasing discharge of contaminating nutrients, *e.g.* phosphate, into the aquatic system has resulted in serious environmental problems around the world, such as eutrophication and consequently algal bloom [1]. Hence, it is necessary to decrease the concentration of phosphate in wastewater before its discharge. The typical discharge limit for phosphorus in wastewater is less than 1 mg P/L [2]; however, this still causes the problem of eutrophication. Therefore, methods which are capable to remove phosphate efficiently and rapidly at a relatively low concentration are urgently needed. A series of methods have been studied to remove phosphate from water [3], in which the adsorption-based process has attracted great interest, due to the high removal efficiency and fast removal rate, especially at low phosphate concentrations [4]. Among various types of adsorbents, including inorganic, organic and inorganic–organic hybrid materials [5–7], well-ordered mesoporous silica materials are useful in adsorption for their unique features, such as highly ordered structures, ultrahigh surface areas, narrow mesopore size distributions, and tunable pore size and structure [8,9]. However, the pure mesoporous silicas exhibit extremely low or even immeasurable phosphate adsorption capacities, which are attributed to the poor capacity of surface groups Si–OH capturing phosphate anions from aqueous solution [10]. So far, organic-functionalization has been considered as an effective strategy to precisely control the chemical properties of silica materials and generate specific binding sites for phosphate ions, which can enhance the adsorption capacity and removal rate of resulting adsorbents. For example, Chouyyok and co-workers reported that Fe(III)-coordinated ethylenediamine-functionalized MCM-41 silica had a phosphate adsorption capacity of 14.13 mg P/g with 99% of phosphate removal within 1 min [9]. Zhang et al. utilized Fe(III) and La(III)-coordinated diamino-functionalized MCM-41 adsorbents for phosphate removal, which showed the maximum adsorption capacities of 16.90 mg P/g and 17.72 mg P/g, respectively [11,12]. Recently, we reported the synthesis of functionalized SBA-15 adsorbents with various loadings of diamino group *via* a new NH_4F-assisted co-condensation method for the first time [13]. With 0.5:1 molar ratio of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane and tetraethoxysilane, the resulting Fe(III)-coordinated sample showed the maximum phosphate capture capacity of 20.7 mg P/g and reached almost 90% of the final adsorption capacity in 10 min.

However, it is noted that the attachment of functional groups on the silica pore surfaces decreased pore sizes of mesoporous silica and subsequently limited the diffusion [14]. Previous research has shown that the introduction of macropores into

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mesoporous materials may act as rapid transport conduits to the active sites on the surfaces of mesopores, thus favoring mass transfer and reducing transport limitations [15]. The objective of our work is to investigate the utilization of Al(III)-coordinated diamino-functionalized macroporous–mesoporous SBA-15 silica material for phosphate removal. Herein, a dual-templating approach was applied to generate mesopores and macropores by using P123 and polystyrene beads in the preparation of adsorbent. Afterwards, the diamino-functional groups were post-grafted onto the macroporous–mesoporous SBA-15 supports, followed by the immobilization of Al(III) active sites. The fabrication, characterization and phosphate adsorption performance of Al(III)-coordinated diamino-functionalized macroporous–mesoporous SBA-15 silicas are detailed in this paper. The presence of interconnected macroporous and mesoporous structures in our prepared adsorbent is expected to promote mass transfer and enhance phosphate removal.

2. Experimental

2.1. Preparation and characterization of adsorbents

Monodispersed polystyrene (PS) beads with an average size of 380 ± 10 nm were synthesized *via* the emulsion polymerization approach as reported [16]. Macroporous–mesoporous SBA-15 silica was prepared with the use of Pluronic P123 triblock co-polymer (PEO_{20}-PPO_{70}-PEO_{20}, Aldrich) and our prepared PS beads as templates which generated mesopores and macropores [17]. 1.0 g of P123 was dissolved in a solution consisting of 7.5 mL of deionized (DI) water and 25.0 mL of 2.0 M HCl under stirring at 35 °C. After well dispersing 8.7 g of PS beads, 2.3 mL of tetraethoxysilane (TEOS, Aladdin Reagent Inc., 95%) was added to the mixture, which was continuously stirred at 35 °C for 24 h and subsequently reacted at 100 °C for another 24 h. Solid powder was filtered and washed with DI water 3 times, followed by calcination in air at 550 °C for 6 h to remove P123 and PS beads. Afterwards, the resulting silica sample was functionalized *via* the post-grafting method, by refluxing in the mixture of 30.0 mL of toluene and 3.0 mL of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPTS, 95%, Aladdin Reagent Inc.) at 130 °C for 24 h. Following that, the diamino-functionalized sample was filtered, washed with ethanol 3 times and mixed in 0.1 M $AlCl_3$ aqueous solution for 2 h. The solid was separated, washed with DI water and 2-propanol, and dried under vacuum at 60 °C for 12 h. The final product, Al(III)-coordinated diamino-functionalized macroporous–mesoporous silica, is denoted as MM-SBA. For comparison, by using the similar synthetic method, the Al(III)-coordinated diamino-functionalized mesoporous silica which was fabricated without the addition of PS beads is denoted as M-SBA.

Surface morphologies of samples were examined by scanning electron microscopy (SEM, JSM-7401F, JEOL Ltd., Japan) and transmission electron microscopy (TEM, JEM2010-HR, JEOL Ltd., Japan). X-ray powder diffraction (XRD) patters were recorded in the 2θ range of 0.6–6° at a scan speed of 1°/min by using a diffractometer (Bruker D8 Advance diffractometer, Germany) with Cu Kα radiation (40 mA, 45 kV). Fourier transform infrared (FT-IR) measurements were performed between 400 cm^{-1} and 4000 cm^{-1} by using Shimadzu IR Prestige-21 instrument, in which KBr pellets containing 0.50% of the samples were used. Nitrogen adsorption–desorption isotherms were measured at 77 K using ASAP2010 (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 ($P/P_0 = 0.05$–0.20). The pore size (D_{BJH}) was calculated from the desorption branch of isotherm by using Barrett–Joyner–Hallenda (BJH) method. The total pore volume (V_{Total}) was evaluated from the adsorbed nitrogen amount at a relative pressure 0.98.

2.2. Phosphate adsorption of adsorbents

A series of batch tests were conducted to investigate the phosphate adsorption performances of adsorbents. In the equilibrium experiment, 0.025 g of adsorbents were added into 25.0 mL of phosphate solutions with various initial concentrations in polypropylene bottles, which were prepared by dissolving anhydrous K_2HPO_4 (analytical grade, Sinopharm Chemical Reagent Co., Ltd) in DI water. After shaking for 2 h, the solutions were removed by filtering through syringe nylon-membrane filters (pore size 0.45 μm; Shanghai Xinya Purification Devices Factory). The concentrations of phosphate in filtrates were analyzed by Autoanalyzer 3 (Bran and Luebbe Inc., Germany). The amount of phosphate adsorbed on the sample at equilibrium (q_e) was calculated by Eq. (1),

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

where C_0 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 well-known Langmuir and Freundlich isotherm models, as shown in Eqs. (2) and (3), respectively [18],

$$\text{Langmuir model}: \quad \frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{C_e}{q_0} \tag{2}$$

$$\text{Freundlich model}: \quad \log\ q_e = \log\ K_F + \frac{1}{n} \log\ C_e \tag{3}$$

where q_0 (mg/g) and K_L (L/mg) are constants in the Langmuir isotherm model which are related to maximum adsorption capacity and energy or net enthalpy of adsorption, respectively; K_F (mg/g) and n are the constants in the Freundlich isotherm model, which measure the adsorption capacity and intensity, respectively.

The adsorption kinetic experiment was conducted as follows: 0.10 g of adsorbent was added in 100.0 mL of phosphate solution with initial concentration of 50.0 mg P/L. The sealed polypropylene bottle was then placed in the shaker bath for 4 h. About 2.0 mL of suspension was taken out of bottle over a given period of time, and the phosphate concentration was analyzed as in the equilibrium experiment.

3. Results and discussion

3.1. Characterization of adsorbents

The X-ray diffraction patterns of M-SBA and MM-SBA are presented in Fig. 1. In the XRD pattern of M-SBA, three well-resolved SBA-15 reflections, one intense diffraction peak (1 0 0) and two relatively weak diffraction peaks (1 1 0) and (2 0 0), suggest the presence of well-ordered hexagonal arrangement of mesoporous silica framework [19]. In the XRD pattern of MM-SBA, the characteristic reflections of SBA-15 peaks are relatively lower; however, all the peaks are distinguishable. This indicates that the synthesized MM-SBA adsorbent has a well-ordered hexagonal mesoporous silica framework as well.

Fig. 2 shows FT-IR spectra of M-SBA and MM-SBA. The bands at 1082 cm^{-1}, 803 cm^{-1}, and 466 cm^{-1} are attributed to the Si–O–Si asymmetric and symmetric vibrations of condensed silica network. The peak at 961 cm^{-1} is ascribed to the non-condensed silanol Si–OH groups [20,21]. The bands observed at 1408 cm^{-1} and 1635 cm^{-1} are corresponding to the NH_2 vibrations [21,22], which confirms the successful incorporation of organic functional groups into the synthesized adsorbents *via* the post-grafting method.