



## Zirconia functionalized SBA-15 as effective adsorbent for phosphate removal

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### ABSTRACT

Phosphate adsorbents with molecular level dispersions of surface functionalities were prepared by covalent grafting of ZrO<sub>2</sub> onto SBA-15. The synthetic adsorbents were characterized by X-ray diffraction, N<sub>2</sub> adsorption/desorption, transmission electron microscope, UV–Vis diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy and zeta-potential measurements in terms of surface chemistry and pore structure, and their adsorption properties toward phosphate were examined. All adsorption isotherms could be well described by the Freundlich model. Compared with SBA-15, markedly enhanced phosphate adsorption was observed on ZrO<sub>2</sub> functionalized SBA-15, which was attributed to a combined effect of high surface exposure of the Zr–OH group and its strong inner-sphere complexing ability for phosphate. Phosphate adsorption was affected by the pH and ionic strength, wherein the adsorption capacity of the adsorbent increased at low pH and high ionic strength. Additionally, the adsorption process obeyed the pseudo-second-order kinetics and the rate constant decreased with initial phosphate concentration. Findings in this study highlight the potential of using functionalized SBA-15 with highly dispersed ZrO<sub>2</sub> as an effective adsorbent for phosphate removal.

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### 1. Introduction

The presence of excessive nutrients (nitrogen and phosphorus) may cause eutrophication of lakes, lagoons, rivers and sea [1]. As one of the nutrients for water eutrophication, phosphate can be released from many non-point and point sources, such as agricultural fertilizers, municipal wastewater, and effluents from chemical and mineral processing industries [2]. Due to more stringent legislation for phosphate discharge, it is thus highly desirable to develop effective treatment methods for phosphate removal from phosphate bearing wastewater prior to its discharge into the aquatic environment.

Adsorption method has been recognized as a simple approach to remove phosphate in water. A variety of metal hydroxides were found to be effective in adsorption of phosphate [3–5]. Among the metal hydroxides, zirconium hydroxide is a superior adsorbent due to its strong surface complexing ability for phosphate and high chemical stability under acidic and basic conditions. For example, Chitrakar et al. [6] reported much higher adsorption capacity of phosphate on zirconium hydroxide than that on layered double hydroxides. Liu et al. [7] attributed the adsorption of phosphate on mesoporous ZrO<sub>2</sub> to a mechanism of anion exchange with surface Zr–OH groups.

Alternatively, dispersion of metal hydroxides over inert supports with high surface areas is an effective method to enhance the adsorption capacities of active species. Liao et al. [8] prepared ZrO<sub>2</sub>-loaded collagen fiber and observed effective phosphate removal over the adsorbents. In parallel, Yuchi et al. [9] studied phosphate adsorption over ZrO<sub>2</sub>-loaded polymer gel and found that the adsorbent was effective for the removal of phosphate at a sub ng ml<sup>-1</sup> level. Notably, in most cases the active ZrO<sub>2</sub> moieties of supported adsorbents exist in nano-particles; accordingly, only ZrO<sub>2</sub> surface is accessible and acts as active adsorption sites. Hence, it is speculated that loading of ZrO<sub>2</sub> moieties on support surface via chemical bonding likely provides a molecular level dispersion of ZrO<sub>2</sub> functionality, giving rise to high surface exposure of adsorption site and thus high adsorption capacity for phosphate.

Since first synthesized in 1992 [10,11], mesoporous SiO<sub>2</sub> has attracted widespread interest due to its large surface area, high pore volume and ordered mesostructure. Because mesoporous SiO<sub>2</sub> matrix is inert in nature, surface functionalization may further extend its applications in adsorption, separation and catalysis [12–14]. Moreover, mesoporous SiO<sub>2</sub> has abundant surface silanol groups, which are susceptible to surface functionalization [13,14]. Considering the high complexing ability of ZrO<sub>2</sub> toward phosphate, it is hypothesized that ZrO<sub>2</sub> functionalized mesoporous SiO<sub>2</sub> prepared by the covalent grafting method may have high exposure of surface functionality and display superior performance for phosphate adsorption. However, thus far few studies have been conducted.

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The objective of this study is to explore the feasibility of ZrO<sub>2</sub> functionalized SBA-15 adsorbents for adsorptive removal of phosphate in water. ZrO<sub>2</sub> functionalized SBA-15 adsorbents were prepared by the post-grafting method, and were characterized by X-ray diffraction (XRD), infrared spectroscopy (IR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), N<sub>2</sub> adsorption/desorption, and zeta potential measurements. Phosphate adsorption to the adsorbents was investigated using the batch technique.

## 2. Experimental

### 2.1. Material preparation

SBA-15 was prepared using Pluronic P123 as the structure-directing agent and tetraethoxysilane (TEOS) as the silica source [15]. Briefly, 8.0 g of Pluronic P123 (Aldrich) was dissolved in 300 ml of 2.0 M HCl solution at 40 °C and 17.6 g of TEOS (98%, Shanghai Chemical Co.) was then added. The final molar composition of the gel mixture was P123:HCl:H<sub>2</sub>O:TEOS = 1:60:10073:435. After stirring at 40 °C for 24 h the solution was transferred to a Teflon-lined autoclave which was kept at 100 °C for 24 h. The resulting material was recovered by filtration, washing repeatedly with distilled water. The organic template (Pluronic P123) was removed by calcination at 550 °C for 6 h in air.

ZrO<sub>2</sub> functionalized SBA-15 was prepared by the post-grafting method [16,17]. Briefly, 2.0 g of SBA-15 was suspended in 40.0 ml of dried toluene, to which 3.1 ml of 70% zirconium isopropoxide (Zr(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>) solution in propanol (Aldrich) was added. The suspension was then refluxed at 110 °C for 3 h. After configuration, the resulting material was washed with toluene, ethanol and distilled water, following by vacuum drying at 110 °C for 12 h. Two- or three-cycle functionalization of SBA-15 was conducted by repeating the above described procedure two or three times. The samples prepared by single-, two- and three-cycle functionalization are denoted as SBA-15-Zr1, SBA-15-Zr2 and SBA-15-Zr3, respectively.

For comparison, ZrO<sub>2</sub> was prepared by the precipitation method [18]. Briefly, 400 ml of 0.5 M ZrOCl<sub>2</sub>·8H<sub>2</sub>O aqueous solution was added dropwise to 150 ml of 2.0 M ammonia solution under vigorous stirring followed by aging at room temperature for 2 h. ZrO<sub>2</sub> was obtained by filtration, repeated washing with distilled water, drying at 105 °C for 6 h, and calcination at 400 °C for 4 h.

### 2.2. Adsorbent characterization

XRD patterns were collected in a range of 0.6–5° for small-angle XRD and 10–80° for wide-angle XRD from a Rigaku D/max-RA power diffraction-meter using Cu K $\alpha$  radiation. TEM images of the samples were recorded with a JEM-200CX electron microscope. N<sub>2</sub> adsorption/desorption isotherms were obtained on a Micrometrics ASAP 2020 apparatus at –196 °C (77 K). ZrO<sub>2</sub> contents in the samples were determined on an ARL9800XP X-ray fluorescence (XRF) spectrometer. The UV–Vis spectra of the samples were collected on a SHIMADU UV-2401PC UV/Vis spectrometer using BaSO<sub>4</sub> as the reference. XPS analysis was performed on a PHI 550 ESCA/SAM X-ray photoelectron spectroscopy equipped with a monochromatized Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV). The C 1s peak (284.6 eV) was used for the calibration of binding energy values. To verify the distribution of ZrO<sub>2</sub> in the samples, the ion sputtering model was used in XPS measurement with Ar as the ion source, under 1000 eV and middle speed sputtering 60 s. The surface zeta potentials of the samples were measured using a Zeta Potential Analyzer (Zeta PALS, Brookhaven Instruments Co.).

The IR spectra of the samples were recorded at 4 cm<sup>–1</sup> resolution using a Nicolet 380 FTIR spectrometer in a vacuum IR system.

The sample was pressed into a self-supporting wafer which was placed in an IR cell connected to a vacuum system. The sample was activated under vacuum (<2 × 10<sup>–5</sup> mbar) by heating to 300 °C at a rate of 10 °C min<sup>–1</sup> and held at this temperature for 4 h. After cooling to 50 °C, IR spectra were collected.

### 2.3. Phosphate adsorption

Phosphate adsorption isotherms were determined by batch adsorption experiments. Briefly, 20.0 mg of adsorbent was introduced into 40 ml glass vials with polytetrafluoroethylene-lined screw caps receiving 40 ml of phosphate solution with varied initial concentrations. The initial pH of phosphate solution was adjusted using 0.1 M HCl to assure the final pH close to 6.2. The samples were shaken by an orbital shaker at 25 °C for 72 h. The time period was sufficient to reach apparent adsorption equilibrium (no further uptake) based on preliminarily determined adsorption kinetics (data not shown). After filtration using 0.45  $\mu$ m filters, the residual phosphate concentration was determined using UV–Vis spectrometry according to the molybdenum blue method with a detecting wavelength of 700 nm [9,19]. The equilibrium adsorption amount of phosphate was calculated according to Eq. (1):

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

where  $q_e$  is the equilibrium adsorption amount,  $C_0$  is the initial phosphate concentration,  $C_e$  is the equilibrium concentration,  $V$  is the solution volume and  $m$  is the adsorbent mass.

The effect of ionic strength on phosphate adsorption to SBA-15-Zr2 was investigated in the presence of NaCl solutions with varied concentrations (0–0.1 mol l<sup>–1</sup>) at pH 6.2 and 25 °C. Separate sets of experiments were conducted to test the effects of pH on phosphate adsorption to the sorbents. In the pH experiments, the initial pH of phosphate solution was preadjusted using 0.1 M HCl and 0.1 M NaOH and the pH of all samples was measured after adsorption equilibrium. All sorption experiments were conducted in duplicate.

### 2.4. Phosphate adsorption kinetics

Phosphate adsorption kinetics was carried out at initial concentrations of 5.0, 12.5 and 30.0 mg P l<sup>–1</sup>. Briefly, 0.25 g of SBA-15-Zr2 was added into a flask containing 500 ml of 5.0, 12.5 or 30.0 mg P l<sup>–1</sup> phosphate solution, which was strongly stirred in an incubator at 25 °C. During the adsorption process, about 2.5 ml of sample was withdrawn at preset time intervals. After fast filtration using 0.45  $\mu$ m filters, the residual concentration of phosphate in the solution was determined spectrophotometrically. The adsorption amount was calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where  $q_t$  is the adsorption amount at time  $t$ ,  $C_0$  is the initial phosphate concentration,  $C_t$  is the concentration at time  $t$ ,  $V$  is the volume of phosphate solution and  $m$  is the adsorbent mass.

## 3. Results and discussion

### 3.1. Material characterization

The wide- and small-angle XRD patterns of SBA-15, SBA-15-Zr1, SBA-15-Zr2 and SBA-15-Zr3 are presented in Fig. 1. In the wide-angle XRD patterns of SBA-15 and SBA-15-Z1, only wide diffraction peaks were observed with  $2\theta$  around 23°, characteristic of amorphous SiO<sub>2</sub> [20]. Increasing ZrO<sub>2</sub> amount led to a shift of the wide diffraction peak to higher  $2\theta$ , reflecting that amorphous ZrO<sub>2</sub> moieties are dominant on SBA-15 surface. Moreover, after calcina-

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