



Controllable synthesis of mesoporous alumina with large surface area for high and fast fluoride removal



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ABSTRACT

Gamma phase of mesoporous alumina (MA) with large surface area was successfully synthesized by a facile hydrothermal method followed by thermal treatment for fluoride removal. The as-synthesized MA nanoparticles with average size of 20 nm–150 nm have ordered wormhole-like mesoporous structure. The pore size is 5 nm with a narrow distribution, and the specific surface area reaches $357 \text{ m}^2 \text{ g}^{-1}$ while the bulk density is $0.45 \text{ cm}^3 \text{ g}^{-1}$. Glucose as a small-molecule template plays an important role on the morphology, surface area and pore diameter of the MA. As an ionic adsorbent for fluoride removal, the maximum adsorption capacity of MA is 8.25 mg g^{-1} , and the remove efficiency reaches 90% in several minutes at pH of 3. The Langmuir equilibrium model is found to be suitable for describing the fluoride sorption on MA and the adsorption behavior follows the pseudo-second-order equation well with a correlation coefficient larger than 0.99. The larger surface area and relatively narrow pore size of MA are believed to be responsible for improving the adsorption efficiency for fluoride in aqueous solution.

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1. Introduction

Fluoride is one of the essential trace elements for growth and development in human body, which has important effect on bone metabolism. However, excessive intake of fluoride will lead to many bone diseases such as brittle bones, osteoporosis, arthritis, cancer and mottling of the teeth, etc. [1,2]. In addition, high concentration of fluoride in groundwater is a worldwide problem, which is not only detrimental to human health but also brings serious environmental pollution [3,4]. Therefore, it is necessary to find out the suitable methods to remove excess fluoride ions in water. The traditional techniques to remove fluoride include chemical precipitation, membrane processes, ion exchange and adsorption [5,6]. Among various methods for defluorination of water, adsorption is an ideal and the most promising method compared to other techniques due to the convenience of operation, lower cost and being a relatively more environment friendly process [7,8]. As a kind of traditional material, MAs have considerable applications in catalysis, adsorption, ceramics, heat insulating and sensing fields [5,9–11] owing to their large surface area, unique pore size distribution, acid-base properties and low price. Using as

a significant adsorbent, the adsorption performances of alumina largely depend upon their crystalline structures and structural properties. Therefore, it is crucially important to prepare alumina with excellent pore structures. Although researchers have fabricated lots of high efficient metal composites for defluorination recently, such as Fe-Mg-La [12], Ce-Fe [13], Ca-Al-La [14], Al-Zr [15], the preparation processes are always complicated and cost is quite high. Therefore, to prepare and regulate the microstructure of alumina ceramics is still the focus of current research.

At present, a considerable volume of MAs have been successfully synthesized by adopting nanocasting method [16,17], solvent-deficient synthesis technique [18,19] and sol-gel process [20]. Great efforts have also been devoted to synthesizing MAs by employing surfactants as templates. For example, Wu et al. [21] synthesized the MA with tunable structural properties via hydrolysis of aluminum isopropoxide associated with non-ionic block copolymer P123 as the structure-directing template. Itoh et al. [22] developed the polyol synthesis of γ -alumina particles utilized flux reaction of ethylene glycol with aluminum nitrate hexahydrate and poly (vinylpyrrolidone) (PVP). MAs synthesized by template methods have larger surface area as well as well-organized mesopore structure [23,24], which can greatly enhance the adsorption capacity of fluoride ions in water. However, the surfactants introduced into the synthesis process are always

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expensive organic macromolecular compounds, which are complicated in the treating process and serious environmental hazardous. Nowadays, some small molecules templates have attracted more attention to fabricate micro- and mesoporous materials due to their facility of preparation and surface modifications [25]. More than that, they also can construct multistage orderly pore structures and regulate the structures, morphologies and surface chemical properties of materials effectively. For instance, saccharide molecules have been utilized to prepare mesoporous silica [26]. To our best knowledge, there are few reports to study the effect of glucose on the structural properties of alumina ceramics materials.

In the present work, we carried out the synthesis of MA by hydrolyzing inorganic Al resources in aqueous solution using glucose as a small molecule template. The resultant sample has large surface area and ordered wormhole-like pore structures. The sorption experiments like adsorption kinetics, adsorption isotherm and the effects of pH on fluoride removal have been investigated in a batch model.

2. Experimental

2.1. Chemicals

Glucose monohydrate ($C_6H_{12}O_6 \cdot H_2O$, CAS: 14,431-14-7), sodium metaaluminate ($NaAlO_2$, CAS: 1138-49-1) and aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, CAS: 7784-13-6) were purchased from Simopharm Chemical Reagent Co., Ltd (China). Sodium fluoride (NaF , CAS: 7681-49-4) was obtained from Aladdin Industrial Corporation, and absolute ethyl alcohol (C_2H_5OH , CAS: 64-17-5) was provided by Tianjin Yongda Chemical Reagent Co., Ltd (China). All chemicals were of analytical purity (except $NaAlO_2$, CP) and used as received without further purification. Deionized water was used for all experiments.

2.2. Material Preparation

Deionized water of 70 mL was added to 5.0 mmol glucose under stirring in a beaker. After 10 min, 10 mmol $AlCl_3 \cdot 6H_2O$ and 10 mmol $NaAlO_2$ were added successively and the mixture was stirred continuously for another 30 min. Then the mixture was transferred into a 100 mL Teflon lined steel autoclave and maintained at 150 °C for 12 h. After being cooled to ambient temperature, a brown solid was obtained and washed with deionized water and anhydrous ethanol for several times and finally dried in an oven at 80 °C overnight.

The dried as-synthesized product was further calcined for 4 h at a 2.2 °C/min heating rate in Muffle furnace at 550 °C under air atmosphere to get $\gamma-Al_2O_3$ (CAS: 1344-28-1) adsorbent. In order to study the effects of quantity of glucose on the structural properties of MA, a series of contrast experiments were also carried out following the above procedures.

2.3. Adsorption tests

The fluoride stock solution of 100 mg L⁻¹ was prepared by dissolving 0.2210 g NaF in 1000 mL deionized water and stored in a polypropylene bottle. Working fluoride anions solutions were obtained by diluting the stock solution to a certain concentration with deionized water suitably.

To test the effect of pH on fluoride removal, 50 mL of 60 mg L⁻¹ sodium fluoride was mixed with 250 mg as-synthesized MA in a 100 mL polyethylene plastic bottle, capped tightly and placed on an automatic shaker (Aohua THZ-82A, Changzhou, China) under shaking at 25 °C. Then the solution was filtered and the fluoride

concentration was analyzed by an ion chromatography (ISC-5000+, Fisher Scientific, USA). The pH of solution was adjusted by adding 0.1 M NaOH (CAS: 1310-73-2) or 0.1 M HCl (CAS: 7467-01-0) solution, and the initial and final pH values were measured by pH meter (SevenMulti, Mettler Toledo, Switzerland).

For adsorption kinetic tests, 250 mg of as-synthesized MA was added to 50 mL of 60 mg L⁻¹ sodium fluoride (without pH adjustment) under stirring for a specified time. The experimental data obtained from batch experiments were fitted to pseudo-first-order and pseudo-second-order kinetic models. Isothermal adsorption experiments were conducted by varying the concentration of sodium fluoride (without pH adjustment) from 10 to 100 mg L⁻¹. The polyethylene plastic bottles were kept in an automatic shaker for 4 h to reach the equilibrium of the solution with the solid mixture. Langmuir and Freundlich isotherm models were used to fit the equilibrium data of fluoride adsorption on the samples.

2.4. Materials characterization

XRD diffraction patterns of the samples were recorded on X'pert Pro X-ray diffractometer (Philips, the Netherlands) to identify their crystal structures. Copper K_{α} radiation ($\lambda=0.15406$ nm) was used with a power setting of 40 kV and 35 mA (Scan rate = 5° min⁻¹). SEM tests were performed on a JSM-5610LV/INCA microscope (JEOL, Japan) with Au-sputtered specimen operated at 15 keV to observe the morphologies of the samples. TEM photographs were obtained on a JEM-2100 microscope (JEOL, Japan) operated at 200 kV. Samples were finely ground in an agate mortar to fine particles and dispersed ultrasonically in ethanol. The well dispersed samples were deposited on a Cu grid covered by a holey carbon film for measurements. Nitrogen adsorption-desorption isotherms were conducted on a Quantachrome Autosorb-iQ apparatus (Quantachrome, USA) at -196 °C. The specific surface areas were calculated by using the Brunauer-Emmett-Teller (BET) method over the relative pressure range of 0.05–0.30, and the pore size distributions (PSD) were calculated from the adsorption branch of the isotherm with the Barrett-Joyner-Halenda (BJH) model.

3. Results and discussion

3.1. Adsorbent characterization

The crystalline phase of as-synthesized MA is identified by XRD. Fig. 1 shows the XRD patterns of the prepared Al_2O_3 . The diffraction peaks at 2θ of 67°, 60.9°, 45.8°, 39.5°, 37.6°, 31.9° and 19.4° correspond to the reflection from (440), (511), (400), (222), (311), (220) and (111) planes in cubic phase of $\gamma-Al_2O_3$ (JCPDS-10-0425) [27], respectively. No other diffraction peaks representing other phases were detected, which indicates a high purity of the prepared samples. In addition, when glucose was not added to the reaction system, the $\gamma-Al_2O_3$ displays a relatively sharper diffraction peaks (shown in Fig. 1a), which presents a better crystallinity than other aluminas templated by glucose. The results show that the amount of glucose almost has no effect on the crystalline phase and the crystalline degree of gamma-alumina.

Fig. 2 shows the SEM images of $\gamma-Al_2O_3$ prepared by adding a certain amount of glucose. When glucose was not added to the reaction system, gamma alumina presents irregular and agglomerated nanoparticles morphology and mingles with some tiny fibers (Fig. 2a). While a series of glucose with different concentration (1.0 mmol, 2.5 mmol, 4.0 mmol and 5.0 mmol) was added to the double hydrolysis reaction system, the final products take on various morphologies as following: sheet-like (Fig. 2b), flower-like

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