Journal of Colloid and Interface Science 475 (2016) 17–25

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Development of a nanosphere adsorbent for the removal of fluoride from water

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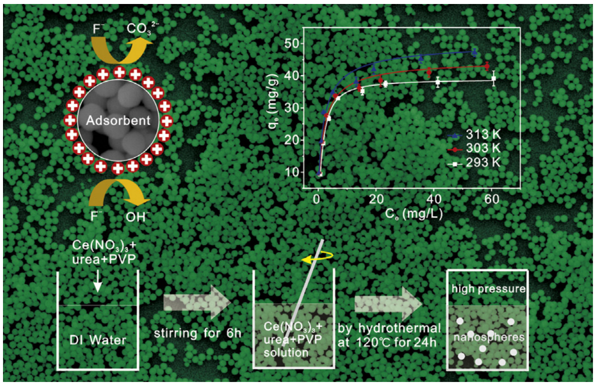
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 February 2016
Revised 15 April 2016
Accepted 22 April 2016
Available online 24 April 2016

Keywords:
$CeCO_3OH$ nanospheres
Fluoride
Adsorption
Carbonate

ABSTRACT

A new uniform-sized $CeCO_3OH$ nanosphere adsorbent was developed, and tested to establish its efficiency, using kinetic and thermodynamic studies, for fluoride removal. The results demonstrated that the $CeCO_3OH$ nanospheres exhibited much high adsorption capacities for fluoride anions due to electrostatic interactions and exchange of the carbonate and hydroxyl groups on the adsorbent surface with fluoride anions. Adsorption kinetics was fitted well by the pseudo-second-order model as compared to a pseudo-first-order rate expression, and adsorption isotherm data were well described by Langmuir model with max adsorption capacity of 45 mg/g at pH 7.0. Thermodynamic examination demonstrated that fluoride adsorption on the $CeCO_3OH$ nanospheres was reasonably endothermic and spontaneous. Moreover, the $CeCO_3OH$ nanospheres have less influence on adsorption of F^- by pH and co-exiting ions, such as SO_4^{2-}, Cl^-, HCO_3^-, CO_3^{2-}, NO_3^- and PO_4^{3-}, and the adsorption efficiency is very high at the low initial fluoride concentrations in the basis of the equilibrium adsorption capacities. This study indicated that the $CeCO_3OH$ nanospheres could be developed into a very viable technology for highly effective removal of fluoride from drinking water.

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http://dx.doi.org/10.1016/j.jcis.2016.04.037
0021-9797/

1. Introduction

Fluoride can be present in drinking water, and it is considered beneficial at levels about 0.7 mg/L but hazardous if it exceeds 1.5 mg/L recommended by World Health Organization (WHO) [1]. Over the past decades, great efforts have been dedicated to searching for efficient alternative materials to improve their fluoride-adsorption capacity in water treatment [2]. Various materials, including layered double hydroxides [3,4], hydroxyapatite [5–7], activated alumina [8–10], zeolites [11,12] and ion-exchange resins [13,14], have been developed for the removal of fluoride. Among these materials, activated alumina is the most common adsorbent for defluoridation, but its disadvantages such as aluminum dissolution and relatively low adsorption capacity prevent it from wide application [15].

To increase the adsorption capacity of fluoride, rare earth, such as La, Ce or Zr, is usually used to prepare the efficient adsorbents, which is widely used in photocatalysis [16], catalysis [17], fuel cells [18], and especially the area of environmental management due to its special rare earth element properties [19]. For example, a novel Al-Ce hybrid adsorbent was prepared through the co-precipitation method. The defluoridation test demonstrated that high sorption capacity for fluoride was 27.5 mg/g at the equilibrium fluoride concentration of 1 mg/L for pH = 6 [20]. In addition, a granular Mn-Ce oxide adsorbent was prepared via co-precipitation method. Sorption isotherm showed that the sorption capacity of fluoride on the granular adsorbent were 45.5 mg/g at the equilibrium fluoride concentration of 1 mg/L for pH = 6 [21]. Besides, extensive research has been carried out in the design and preparation of nanostructures with different shapes and sizes because of their corresponding novel properties and potential applications for a few decades. CeO_2-ZrO_2 nanocages were prepared by Kirkendall effect, and their fluoride removal performance showed that the Langmuir maximum capacity reached to 175 mg/g and the optimum pH range was 3.5–4.5 [22]. Consequently, cerium compounds showed high removal capacities for fluoride due to its special properties, though these had narrow pH range. In general, anions are adsorbed on metal oxide based nanomaterials through electrostatic attraction and/or ion exchange. Surface hydroxyl groups are mainly reported to be involved in the ion exchange step. However, the synthesis of aluminium carbonate hydroxide nanospheres has been attempted, which had abundant carbonate groups on the surface area, and showed superb adsorption properties for AsO_4^{3-} and $Cr_2O_7^{2-}$ at pH 7, respectively [23]. This study confirmed a new adsorption mechanism involving ion exchange between carbonate groups and AsO_4^{3-} or $Cr_2O_7^{2-}$ species.

Apart from the above mentioned considerations, a one-step preparation without any following modification is regarded as an effective, energy-saving and labour-saving approach, in considering the direct formation of uniform-sized nanospheres during the synthesis process. However, one-step synthetic procedures for the synthesis of monodisperse $CeCO_3OH$ nanospheres are still a challenge because of the difficulty in manipulating the homogeneous nucleation and crystal growth. In this paper, we for the first time synthesized uniform-sized $CeCO_3OH$ nanospheres with a given amount of polyvinylpyrrolidone (PVP) by one-step hydrothermal procedure, which were characterized by SEM, XRD and XPS. Their defluoridation capacity and adsorption kinetics for fluoride were examined. The effects of pH, initial fluoride concentration and co-existing anions were investigated. The results show that the adsorbent possesses wide available pH range, high selectivity and excellent adsorption capacity for fluoride removal at the low initial fluoride concentrations. The fluoride removal mechanism indicated that the fluoride adsorption mainly resulted from the exchange of the carbonate and hydroxyl groups on the surface of the $CeCO_3OH$ nanospheres with fluoride anions and electrostatic interaction.

2. Experimental section

2.1. Synthetic details of the $CeCO_3OH$ nanospheres

All of the chemicals used for the synthesis of the $CeCO_3OH$ nanospheres were of analytical grade, which were received from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Double distilled water was used throughout the experiment. The synthesis of the $CeCO_3OH$ nanospheres was based on a modified method of that investigated by Du et al. [24]. In a typical synthesis protocol, 2.5 mmol of $Ce(NO_3)_3{\cdot}6H_2O$, 37.5 mmol of urea and 12.6 μmol of PVP were dissolved in 90 mL deionized water with vigorous magnetic stirring at room temperature. The mixture was stirred continuously by using a magnetic stirrer for 6 h to form the transparent solution. And then the homogeneous solution was transferred into a 125 ml Teflon-lined stainless steel autoclave and maintained at 120 °C for 24 h. After the autoclave was cooled to room temperature naturally, the precipitates were collected by centrifugation and washed thoroughly with deionized water and ethanol for several times, and dried in an oven at 80 °C for 5 h. Thereafter the final products were characterized.

2.2. Materials characterizations

X-ray diffraction (XRD) patterns were obtained on an X'Pert-ProMPD diffractometer with Cu Ka radiation ($\lambda = 0.15418$ nm) at 40 kV and 200 mA. The scanning electron microscopy (SEM) images were taken by a field-emission scanning electron microscopy (FE-SEM, FEI Sirion 200 FEG, operated at 10 kV). For SEM characterization, 0.2 g $CeCO_3OH$ nanospheres were dispersed in 10 mL absolute ethyl alcohol, and then dripped onto the silica pellet and dried in the air for use. Thermo-gravimetric analysis (TGA) was tested on a SDT-Q600 DTG-TGA instrument by heating rate 10 °C/min in nitrogen flow. The nitrogen adsorption and desorption isotherms with a degassing temperature of 70 °C were carried out with a Micromeritics ASAP 2020 M + C analyzer. The Brunauer-Emmett-Teller (BET) specific surface and pore size distribution of adsorbent were tested by the nitrogen adsorption and desorption isotherms at 78 K. The adsorbent before and after fluoride adsorption was analyzed using X-ray photoelectron spectroscopy (XPS, VG ESCALAB MKII spectrometer, Mg K_α X-ray source, 1253.6 eV, 120 W) and Fourier transform infrared (transmission FT-IR, NEXUS-870 FT-IR spectrometer, KBr pellet) spectra in the range of 4000–400 cm^{-1}. The co-existing anions (bicarbonate, chloride, phosphate, nitrate and sulfate) concentration was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Surface charge measurements were performed on a Zeta Potential Analyzer (DelsaNano C/Z, Beckman, Coulter, USA, electromobility: -1.2×10^{-3} $cm^2/V\,s \sim +1.2 \times 10^{-3}$ $cm^2/V\,s$). Before measurement, 1 mg sample was diluted in 30 mL deionized water with different pH values and ultrasonicated for 3 min.

2.3. Fluoride adsorption

Fluoride anions (F^-) stock solution with a concentration of 1000 mg/L was prepared by dissolving 2.21 g sodium fluoride into 1000 mL deionized water. Fluoride-bearing solutions were obtained by diluting the stock solution to given concentrations with ultrapure water. The pH values were tested by pH electrode pH S-3C (Leici, China). The measurements of fluoride concentration were carried out using expandable ion analyzer with the fluoride