Chemical Engineering Journal 292 (2016) 174–182

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Supercritical carbon dioxide fluid assisted synthesis of hierarchical AlOOH@reduced graphene oxide hybrids for efficient removal of fluoride ions

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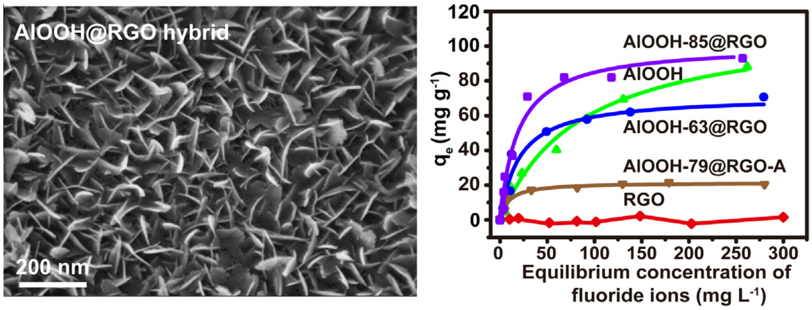
HIGHLIGHTS

- Supercritical CO_2 fluid is used to synthesize AlOOH@reduced graphene oxide hybrids.
- The hierarchical hybrid exhibits excellent defluoridation capacity at low concentrations of fluoride ions.
- The hybrid exhibits a large surface area of 513 $m^2\ g^{-1}$ and a high adsorption capacity of 118.7 $mg\ g^{-1}$.
- The covalently bonded structure of the hybrid affords prominent separability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 December 2015
Received in revised form 28 January 2016
Accepted 3 February 2016
Available online 8 February 2016

Keywords:
Fluoride ion removal
Graphene oxide
AlOOH
Hybrids
Supercritical CO_2

ABSTRACT

Hierarchical AlOOH@reduced graphene oxide (RGO) hybrids are synthesized by an anti-solvent process with the assistance of supercritical carbon dioxide ($scCO_2$) fluid due to its high diffusivity and low viscosity. The presence of RGO allows the uniform and vertical assembling of AlOOH nanosheets to form hierarchically nanostructured hybrids with a large specific surface area of 513 $m^2\ g^{-1}$. The favorable structure with numerous mesopores provides sufficient active sites for the adsorption of fluoride species, leading to a maximum adsorption capacity of 118.7 $mg\ g^{-1}$, which is among the best performances of aluminum based adsorbents. Compared to neat AlOOH, it is interesting that AlOOH@RGO hybrid exhibits a much better defluoridation capacity at lower initial concentrations of fluoride ions, which is quite valuable when considering the low fluoride ion concentrations in contaminated groundwater. The stable and robust hierarchical structure afforded by covalent bonding between AlOOH and RGO further endows the hybrid as a promising adsorbent for practical treatment of wastewater due to its excellent fluoride adsorption capacity and ease of separation from aqueous solutions.

1. Introduction

Fluoride benefits human beings by reducing enamel erosion and preventing osteoporosis at its low concentrations, however, long-term intake of high fluorine water would cause dental and skeletal fluorosis and other diseases [1–4]. Therefore, various methods including chemical precipitation [5], ion exchange [6], electrochemical process [7], and adsorption technique [4,8,9], are developed to remove excess fluoride ions from groundwater for meeting the requirement of drinking water [10,11]. Compared to other approaches, adsorption technique is preferred due to its ease of operation and low cost in removing fluoride from water. Adsorbents with favorable structures, high adsorption capacities, and ease of separa-

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http://dx.doi.org/10.1016/j.cej.2016.02.008

tion are highly desirable. Among the adsorbents used for defluoridation, such as activated carbon [12], metal oxides [13] and aluminum based adsorbents [9,14], aluminum hydroxides receive more attention because of their strong affinity for fluoride and low cost for large-scale production [15]. Nevertheless, aluminum hydroxides present a high tendency to aggregate and show low surface areas, reducing the adsorption capacities toward fluoride ions.

To overcome the abovementioned problem, massive efforts have been made to design aluminum adsorbents with unique architectures and large surface areas. Li et al. [4] prepared highly ordered mesoporous alumina by a sol–gel method, which shows a large specific surface area of 361 $m^2\,g^{-1}$ and high adsorption capacity for fluoride ions. Yang et al. [14] reported disordered mesoporous alumina with high surface area and high defluoridation capacity. However, complicated and tedious synthetic procedures and subsequent calcination process were required. Constructing hierarchical nanostructures is effective to increase specific surface area. Porous aluminum sulfate composites prepared from three-dimensional (3D) graphene hydrogel show a maximum adsorption capacity of 68.9 $mg\,g^{-1}$ due to the high specific surface area (144 $m^2\,g^{-1}$) [8]. Despite the impressive progress, the adsorption capacity for fluoride ions needs to be enhanced further for practical applications, although it is difficult to realize by using conventional approaches.

Recently, eco-friendly supercritical carbon dioxide ($scCO_2$) fluid has been used to synthesize nanostructured aluminum materials due to its advantages, including low viscosity, high diffusivity, zero surface tension, and easily tunable properties [16–18]. Muhammad et al. [19] reported the synthesis of high surface area alumina nanofibers with acetic acid as the polycondensation agent in $scCO_2$ fluid. Very recently, γ-alumina nanosheets were prepared by a hydrothermal process, giving a high specific surface area of 200 $m^2\,g^{-1}$ and a good adsorption capacity for uranyl ions [17]. Although large surface areas show promising defluoridation capacities, relevant research has not been reported. It is expected that assembling of nanostructured aluminum adsorbents on substrates may avoid the aggregation of nanoparticles and bring about excellent separability, leading to large specific surface area and excellent adsorption performance. Graphene oxide (GO) and reduced graphene oxide (RGO) have been used to prepare polymer nanocomposites [20–22] and adsorbents of heavy metal ions and organic dyes [23,24]. However, to the best of our knowledge, there is few literature about the $scCO_2$ fluid assisted synthesis of aluminum hydroxide for the removal of fluoride ions.

Herein, hierarchical AlOOH@RGO hybrids are prepared with the assistance of $scCO_2$ fluid. The advantageous structure provides a large specific surface area (513 $m^2\,g^{-1}$) and numerous active sites available for the adsorption of fluoride species. A high maximum removal capacity of 118.7 $mg\,g^{-1}$ is obtained for AlOOH@RGO hybrid, which is one of the best performances for aluminum based adsorbents. Compared to neat AlOOH, the AlOOH@RGO hybrid exhibits much better defluoridation capacity especially at lower initial concentrations of fluoride ions, which is quite valuable when considering the low fluoride ion concentrations in contaminated groundwater. The covalent bonding between AlOOH and RGO provides an excellent separability of the hybrids for practical application. The adsorption mechanism of the AlOOH@RGO hybrids for fluoride ions is also analyzed.

2. Experimental

2.1. Materials

GO was prepared from natural graphite flakes by a modified Hummers method as reported [25]. $Al(NO_3)_3{\cdot}9H_2O$, NaF and CO_2 gas (99.99%) were bought from J&K Sci. Co., Aladdin-Reagent, and Yanglike Gases, respectively. All of the chemicals were used as received without further purification.

2.2. $scCO_2$ fluid assisted synthesis of AlOOH@RGO hybrids

1.0 g GO and 6.0 g $Al(NO_3)_3{\cdot}9H_2O$ were dispersed in 100 mL ethanol by ultrasonication and the resultant suspension was loaded into a high-pressure autoclave. The autoclave was filled with CO_2 of 6 MPa at 30 °C and then the temperature was increased to 140 °C to reach supercritical state. After vigorous stirring for 12 h, the autoclave was cooled to room temperature and the CO_2 gas was released slowly. The resultant solid product was centrifuged and washed repeatedly with ethanol prior to drying at 80 °C for 24 h. The as-prepared specimen was denoted as AlOOH-XX@RGO hybrid, where XX represents AlOOH content determined by thermogravimetric analysis (TGA). Three hybrids containing 63, 76 and 85 wt% of AlOOH were prepared by controlling the amounts of $Al(NO)_3$ and GO precursors. Both AlOOH and RGO were prepared by a similar procedure. To explain the role of $scCO_2$, another hybrid was also prepared without using $scCO_2$, and denoted as AlOOH-79@RGO-A hybrid.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded using a Bruker AXS D8 advance diffractometer at a scanning rate of 10° min^{-1}. Raman analysis was conducted by a Renishaw in via Raman microscope (Britain) using a laser with an excitation wavelength of 514 nm. TGA was performed with a TA Q50 thermogravimetric analyzer in an air atmosphere at a heating rate of 10 °C min^{-1}. X-ray photoelectron spectroscopy (XPS) was carried out on a ThermoVG RSCAKAB 250X high-resolution X-ray photoelectron spectroscope with Al Kα X-ray radiation as the X-ray source for excitation. The morphology and structure of specimens were observed with a Hitachi S-4800 field emission scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscope (EDX), and a Tecnai G2 F20 S-TWIN high resolution transmission electron microscope (TEM) at 200 kV. Brunauer–Emmett–Teller (BET) surface area and Barret–Joyner–Halenda (BJH) pore size distribution were measured by a Micromeritics ASAP 2460 surface area and a Norcross porosity analyzer (GA) using nitrogen adsorption and desorption. The concentration of Al was measured using an Agilent 7500ce ICP-MS inductively coupled plasma atomic emission spectroscopy. The concentration of fluoride ions was determined by a Thermo Scientific ICS-5000 ion chromatography.

2.4. Batch adsorption measurements

The thick solution of fluoride ions (1000 $mg\,L^{-1}$) was prepared by dissolving 2.210 g NaF in 1000 mL water, which was diluted to solutions of different concentrations (3–350 $mg\,L^{-1}$). To investigate the effect of pH on the defluoridation capacity and dissolution of adsorbents, 20 mg AlOOH-63@RGO hybrid was added into 20 mL solution of fluoride ions (50 $mg\,L^{-1}$) or 20 mL deionized water. The initial pH value of each suspension was carefully controlled between 3 and 11 using 1 M HCl or 1 M NaOH at different time intervals. After stirring for 24 h at 20 °C, the solution was separated from its suspension by centrifugation and filtration, and the separated solution was used for the measurement of fluoride ion concentration and aluminum content. In a similar procedure, the isothermal adsorption and the adsorption kinetics tests were carried out at 20 °C under vigorous stirring. The initial pH value was kept at ~6.5, and the volume of fluoride ion solution and the mass of adsorbent were 20 mL and 20 mg, respectively. To explore the