



High efficient removal of fluoride from aqueous solution by a novel hydroxyl aluminum oxalate adsorbent

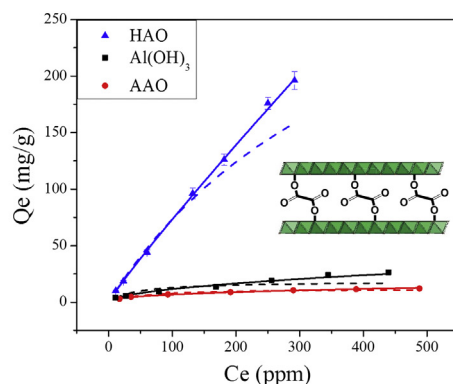
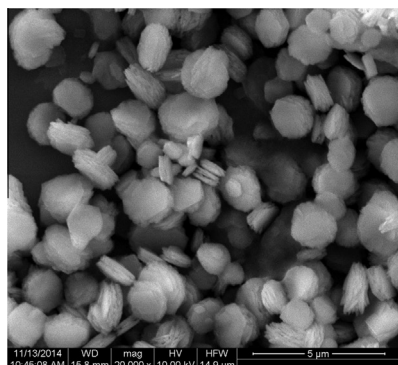


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GRAPHICAL ABSTRACT



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ABSTRACT

A novel adsorbent, hydroxyl aluminum oxalate (HAO), for the high efficient removal of fluoride from aqueous solution was successfully synthesized. The adsorbent was characterized and its performance in fluoride (F^-) removal was evaluated for the first time. Kinetic data reveal that the F^- adsorption is rapid in the beginning followed by a slower adsorption process; 75.9% adsorption can be achieved within 1 min and only 16% additional removal occurred in the following 239 min. The F^- adsorption kinetics was well described by the pseudo second-order kinetic model. The calculated adsorption capacity of this adsorbent for F^- by Langmuir model was 400 mg g^{-1} at pH 6.5, which is one of the highest capabilities of today's materials. The thermodynamic parameters calculated from the temperature-dependent isotherms indicate that the adsorption reaction of F^- on the HAO is a spontaneous process. The FT-IR spectra of HAO before and after adsorbing F^- show adsorption mechanism should be hydroxyl and oxalate interchange with F^- .

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1. Introduction

Fluorine is being used in industrial activities with an increasing amount and then introduced into the aquatic environment in

fluoride (F^-) form as a consequence of its widely use in modern industries. Though fluorine is a trace element necessary to human body for the calcification tooth and skeleton [1], a number of diseases, such as fluorosis of bone and cancer [2], are caused by ingestion of water contaminated with excess fluoride. As with the diseases mentioned above, the best alternative to prevention is keeping from excessive fluoride ingestion. According to WHO

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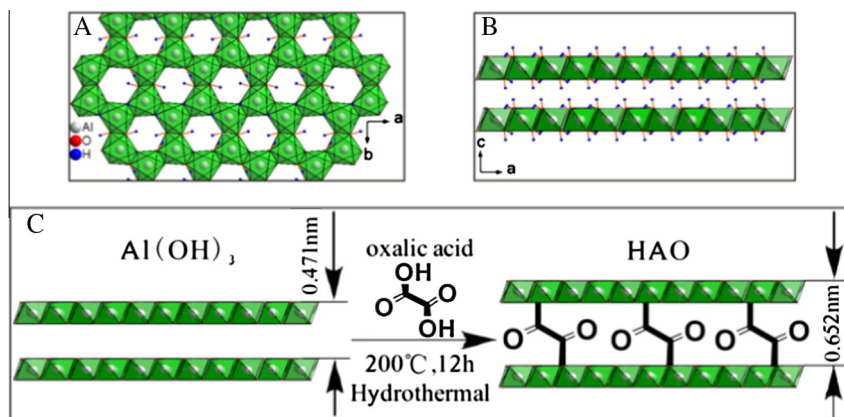


Fig. 1. Structure of $\text{Al}(\text{OH})_3$ layer sheets (A) c-direction view, (B) b-direction view, and diagram of preparation of HAO sorbent (C) oxalate intercalation in $\text{Al}(\text{OH})_3$ interlayer space and diagram of preparation of HAO adsorbent. The green layers represent the sheet made of aluminum-oxygen octahedrons.

(World Health Organization), the permissible upper limit of F^- in drinking water is 1.0 mg L^{-1} [1], and the excessive F^- in the water should be removed.

There are many fluoride waste water treatment methods, including ion exchange [3], reverse osmosis [4], electro dialysis [5], chemical precipitation [6], membrane separation [7], coagulation sedimentation [8], electro coagulation [9] and adsorption processes [10]. Among the methods, adsorption technology is an economical and efficient method for producing high quality of drinking water. In recent years, a variety of adsorbents like activated alumina, chitosan beads, activated carbon, clay, hydroxypatite, etc., have been identified as the promising defluorinating agents [11,12]. However, there is still a great demand for more effective, simple, and low-cost adsorbents for the removal of fluoride.

Recent studies revealed that the intercalated layered materials were widespread attentions due to their excellence adsorption and ion exchange performances for adsorbing metal ions, such as Cu^{2+} , Cd^{2+} , Pb^{2+} and Hg^{2+} , with high selectivity [13–19]. As an important defluorinating material, $\text{Al}(\text{OH})_3$ is also a layered hydroxide material [20]. The layers are made of aluminum-oxygen octahedrons $[\text{Al}(\text{OH})_6]^{3-}$, in which octahedrons share edges, and construct the infinite hexameric ring sheet layer [21]. The layers can be stacked one above the other in different ways, forming four crystallographic forms: bayerite [22], gibbsite [23], nordstrandite [24] and doyleite [25]. Although the intra layer bonding is strong ion covalent, interlayer bonding is weak van der Waal's [20]. So, the interlayer space in $\text{Al}(\text{OH})_3$ should be easy to be intercalated by some light-weight-molecule matters. Some light-weight-molecule agents including pyromellitic acid [13], lactic acid [26], citric acid [27] and malic acid [28] have been successfully used to synthesize the intercalated layered materials.

In this paper, oxalate was selected to intercalate into the interlayer space in $\text{Al}(\text{OH})_3$ by a facile hydrothermal method. The structure of $\text{Al}(\text{OH})_3$ layer sheets and the process of oxalate intercalation in $\text{Al}(\text{OH})_3$ interlayer space was demonstrated in Fig. 1. The oxalate modified $\text{Al}(\text{OH})_3$ was named after hydroxyl aluminum oxalate (HAO) here. The interlayer space in $\text{Al}(\text{OH})_3$ expanded by intercalation and the HAO specific surface area would be increased notably. By the way, $\text{Al}(\text{III})$ on the sheet layer is of good coordination ability toward F^- [29], HAO should be an effective adsorbent for the removal of fluoride from aqueous solution. In present study, the defluorination capacity and adsorption kinetics of the as-prepared HAO for F^- were examined. The effects of pH, initial F^- concentration and co-existing anions were investigated. The results show that the adsorbent possesses high selectivity and excellent adsorption capacity for F^- removal. The F^- removal

mechanism was studied by Fourier transform infrared spectroscopy (FT-IR), indicating that the fluoride adsorption mainly resulted from the exchange of oxalic ions and hydroxyl groups on the surface of the HAO with fluoride anions. We anticipate this work could provide a good example for highly efficient and long-term usage of the HAO during removing fluoride from drinking water.

2. Materials and methods

2.1. Materials

Aluminum isopropoxide (AIP, $\text{Al}[\text{OCH}(\text{CH}_3)_2]_3$, 99.99%) was purchased from Sigma–Aldrich as an aluminum precursor. Oxalate dihydrate (OD, AR), sodium hydroxide (NaOH, AR), nitric acid (HNO_3 , AR), sodium nitrate (NaNO_3 , AR), sodium chloride (NaCl, AR), sodium sulfate (Na_2SO_4 , AR), sodium carbonate (Na_2CO_3 , AR), sodium bicarbonate (NaHCO_3 , AR), sodium phosphate (Na_3PO_4), polyvinyl pyrrolidone (PVP, K30) and sodium fluoride (NaF, AR) were purchased from Shanghai Chemical Reagents Company. Commercial activated aluminum oxide (AAO) was purchased from Shanghai JIADING Molecular Sieve Plant. Ultra-pure water ($18 \text{ M}\Omega$) was produced using a PSDK System (ZIHANSHIJI, Beijing, China). All reagents were used without further purification.

2.2. Preparation of adsorbents

0.01 mol of AIP, 0.4 g PVP and 40 mL ultra-pure water were mixed and stirred at 800 rpm by a magnetic stirrer for 12 h until uniform white suspension was obtained. The white suspension was $\text{Al}(\text{OH})_3$, which was the hydrolysis product of AIP. 0.005 mol of OD were added in the suspension as chelating reagent, and then the suspension was stirred for another 4 h and was transferred to an autoclave, heated at 200°C , and maintained at this temperature for 12 h. White precipitate was obtained in the autoclave and was named after HAO in this paper. The diagram of preparation of HAO adsorbent was showed in Fig. 1. $\text{Al}(\text{OH})_3$ and HAO were washed with ultra-pure water by suction filtration method. Two filter cakes were dried in a vacuum drying oven at 60°C for 12 h and all become white powders which can be used for characterization or adsorption.

2.3. Characterization

X-ray diffraction (XRD) was measured on a D/max2500 with a Cu $\text{K}\alpha$ source ($\lambda = 1.541 \text{ \AA}$). The HAO morphology was investigated

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