

Fluoride adsorption onto amorphous aluminum hydroxide: Roles of the surface acetate anions

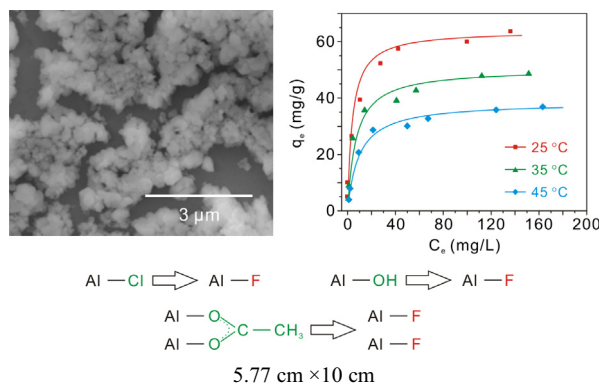


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GRAPHICAL ABSTRACT



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ABSTRACT

Amorphous aluminum hydroxide with hydroxyl groups, acetate anions and chlorine anions enriched surface was synthesized, and was characterized by X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, and nitrogen adsorption-desorption isotherms. Batch experiments were performed to study the influence of various experimental parameters such as contact time, initial fluoride concentration, temperature, pH value and the presence of competing anions on the adsorption of fluoride on amorphous aluminum hydroxide. The kinetic data was well fitted to pseudo-second-order model. The fluoride adsorption on the amorphous aluminum hydroxide can be well described by the Langmuir model, and the maximum adsorption capacity was 63.94 mg g⁻¹ at pH 7.0. Thermodynamic parameters including the Gibbs free energy, standard enthalpy and standard entropy were calculated, and the results suggested that the adsorption of fluoride on the amorphous aluminum hydroxide was a feasible, spontaneous and exothermic process. The adsorption mechanism was revealed by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy analysis. The results suggested that the surface acetate anions and surface chlorine anions played important roles in the fluoride removal process.

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1. Introduction

The occurrence of fluoride in natural ground water is a worldwide problem and has attracted more and more attentions. The WHO guideline of fluoride in drinking water is 1.5 mg L⁻¹ [1].

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Though the presence of fluoride in drinking water is essential for human health, but the excessive intake will result in several diseases, such as dental/skeletal fluorosis, neurotransmitters and fetal cerebral function [2,3]. Thus, several techniques have been developed for fluoride removal, such as ion exchange, precipitation and coagulation, adsorption, membrane separation, reverse osmosis, and electrodialysis [4]. Among these methods, the adsorption method has attracted great attentions in the purification of water with trace levels of fluoride owing to its low cost, easy operation and treatment stability [5].

The adsorption of fluoride was a complex physical and chemical process, and the adsorption performance of the adsorbent were determined by their structures, especially the surface structures. Though soils/clays, minerals, and serials of low-cost adsorbents can removal fluoride [4], but most of them suffered from the low adsorption capacity, narrow available pH range and cannot be regenerated. The low adsorption performance should relate to their inactive surface structures. Thus, the synthesis of new adsorbent with more active surface structures have attracted great attentions. Up to now, several synthetic materials, such as ferric hydroxide [6], 2-Line ferrihydrite [7], ZrO_2 [8], mesoporous aluminas [9], boehmite [10], MgO [11] and CaO [12] have been reported for fluoride removal. The adsorption capacities of iron oxides and boehmite were very low [6,7,10]. Though the adsorption capacity of mesoporous aluminas was higher than that of boehmite and iron oxide, but the formation of the mesoporous structures needs organic polymer template [9]. The price of ZrO_2 is very high, which strictly limited its wide application. For MgO and CaO, the generated corresponding hydroxides will resolve in water and then increase the alkaline of the solution owing to their low stability in aqueous solution [11,12]. Furthermore, many multi-component metallic oxide composites, such as Zr–Fe [13], Mg–Al [14], Ce–Zr [15], Mn–Ce [16], Fe–Al [17], Fe–Ti [18], and Ca–Al [19], and Al–Ce [20] bimetallic oxides, Ca–Al–La [21], Fe–Al–Ce [22], Fe–Al–Cr [23] and Mg–Al–Fe [24] trimetallic oxides have been synthesized owing to their improved fluoride removal properties. The calcium and magnesium contained oxides still suffered from the increased alkaline of the solution after fluoride removal. The rare earth contained adsorbents were obviously suffered from the low abundance. More importantly, among these synthetic adsorbents, the most frequently proposed fluoride removal mechanism is the ion-exchange between the surface hydroxyl group and fluoride ions [6–9,14–16,21,22]. Thus, the improved adsorption properties of them were resulted from the increased content of the surface hydroxyl group. However, based on the Le Chatelier's principle, the removal rate of this type of ion-exchange was definitely suffered from high pH values. Thus, the investigation of new types of surface ion-exchange groups will bring us an opportunity to overcome this disadvantage.

Previously researches have demonstrated that the sulfate-doped Fe_3O_4/Al_2O_3 and aluminum hydroxides can improve the fluoride removal performance compared with the undoped ones [25,26]. Furthermore, in our previous work, we reported that ion-exchange process based on the surface nitrate anions [27,28], the surface carbonate-like species [29,30] and the surface sulfate anions [17,31]. These results mean that many surface anions also can take part in the ion-exchange process besides the surface hydroxyl group. The ion-exchange based on the above surface anions as well as the hydroxyl group can greatly decrease the influence of pH values on the removal rate. Thus, the design of adsorbent with new surface ion-exchange groups should be of importance for both theoretical investigations and practical water treatment applications. In the present work, amorphous aluminum hydroxide, with acetate anions and chlorine anions enriched surface, were synthesized. Fluoride removal potential of the amor-

phous aluminum hydroxide adsorbent was evaluated under various operating conditions such as contact time, initial fluoride concentration, pH, temperature and co-existing anions. The regeneration and recyclability of the amorphous aluminum hydroxide adsorbent were also studied. Moreover, the fluoride removal mechanism was revealed by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The results suggested that both of the surface acetate anions and surface chlorine anions were participated in the ion-exchange process towards fluoride, which would bring forward an important approach to design new types of adsorbent.

2. Materials and methods

2.1. Materials and synthesis

All reagents used were of analytical grade and were purchased from Shanghai Chemical Reagents Company (Shanghai, China) and used without further purification. In a typical synthesis process, 3.62 g of $AlCl_3 \cdot 6H_2O$ were dissolved in 100 mL ethylene glycol (EG). Under vigorous stirring, 3.69 g of sodium acetate anhydrous was added into the above solution, and the mixture was kept stirring for 30 min. Then, the above solution was transferred into a Teflon-lined stainless steel autoclave, sealed and heated to 180 °C for 15 h, then cooled naturally to room temperature. The resulting white precipitates were centrifuged and thoroughly washed with distilled water and absolute ethanol for several times, and finally dried in an oven at 60 °C.

2.2. Characterization

The obtained adsorbent was characterized by X-ray diffraction (X'Pert ProMPD, Cu $K\alpha$ radiation, wavelength 1.54056 Å), field emission scanning electron microscopy (FEI Sirion 200 FEG, operated at 10 kV), transmission electron microscopy (JEOL-2010, operated at 200 kV), Fourier transform infrared spectroscopy (Nicolet Analytical Instruments, NEXUS-870), and X-ray photoelectron spectroscopy (VG ESCALAB MKII spectrometer, Mg KR X-ray source, 1253.6 eV, 120 W) analyses.

2.3. Adsorption experiments

The fluoride stock solution was prepared with deionized water using NaF, and stored in a sealed polypropylene bottle under cool and dark conditions. By appropriately diluting the stock solution to certain concentration with distilled water, working fluoride anions solutions were obtained. The adsorption isotherm was investigated by varying initial fluoride concentration from 5 to 200 $mg L^{-1}$ (5, 10, 30, 50, 80, 100, 160 and 200 $mg L^{-1}$). The experiments were carried out in 15 mL polypropylene flasks containing 10 mL of fluoride solution and 10 mg of adsorbent, and then the flasks were shaken at 150 rpm in a shaker at 25 °C for 24 h. The pH of the solutions was adjusted every 4 h with 0.1 $mol L^{-1}$ HCl or/and NaOH solution to around $pH 7.0 \pm 0.1$ during shaking process. After that, the adsorbent was separated from the solution by centrifugation, and the residual fluoride concentration in solution was measured by the fluoride ion selective electrode (PF-202-CF) by use of total ionic strength adjustment buffer (TISAB) solution (58 g of sodium chloride, 2.94 g sodium citrate, 57 mL of glacial acetic acid and approximately 150 mL of 6 $mol L^{-1}$ NaOH in a volume of 1 L) to maintain pH 5.0 and to eliminate the interference effect of complexing ions [17]. All of the experiments were conducted three times and the averages of the results were used for data analysis. The amount of fluoride adsorbed (q_e in $mg g^{-1}$) was determined by Eq. (1):

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