Research on removal of fluoride in aqueous solution by alumina-modified expanded graphite composite

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ABSTRACT

Amorphous Alumina-modified Expanded Graphite (Al_2O_3/EG) composite was prepared via a facile solution method followed by thermal treatment at 450 °C for 2 h, which was used to remove trace F^- in aqueous solution. Alumina nano-peas (with a diameter of 10–30 nm) were observed on the surface of EG by Field Scanning Electron Microscope (FSEM). The X-ray powder diffraction (XRD) results dominated the Alumina was amorphous. FTIR spectra analysis indicated that Al—F bends appeared after adsorption. The effect of pH and adsorbent dose were studied in a series of batch adsorption experiments. The Effect of pH results showed that the solution pH had no significant effect on F^- removal between pH = 3.0–7.0. The superior adsorbent properties of Al_2O_3/EG proved highly effective in absorbing F^-, where the removal rate reached 94.4% and the adsorption capacity reached 1.18 mg/g. The results showed that Al_2O_3/EG could removed trace amounts of F^- in solution effectively and the residual F^- concentrate could decreased to less than 0.28 ppm. The isotherms and thermodynamics parameters were calculated which displayed that the adsorption was a multi-molecular layer adsorption between the adsorbed molecules, and the process was spontaneous endothermic.

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1. Introduction

Naturally F^- is a major occurring contaminant in drinking water in many regions of the world. Ingestion of F^- within the permissible limit is beneficial to human body for the calcification of dental enamel and maintenance of healthy bones [1]. When F^- is present in excess of 1.5 mg/L [2], it affects the metabolism of elements, such as Ca and P in human body and causes molting of teeth and lesion of endocrine glands, thyroid, liver and other organs [3]. The most common symptom of chronic fluoride exposures is skeletal fluorosis, which can lead to the permanent bone and joint deformations and dental fluorosis. The dental or skeletal fluorosis is irreversible and no treatment exists. The only remedy is prevention by keeping F^- intake within safe limits [4]. According to WHO (World Health Organization), the permissible limit of F^- in drinking water is 1.0 mg/L [5], and the redundant F^- should be removed from drinking water. So, it is imperative and significant to explore the suitable technique to remove excessive F^- from water.

Literatures showed that various methods were suggested for the removal F^- included with nanofiltration [6], electrocoagulation [7], ion exchange [8], reverse osmosis [9], electrodialysis [10], precipitation [11], membrane separation [12], adsorption [13] and some biological processes [14]. The main disadvantage of these methods are the generation of unwanted chemicals, waste disposal issues and low economic viability, high maintenance cost, fouling, scaling, and membrane degradation. Adsorption method is widely accepted technique because it is more effective in reducing F^- concentrations to values well below permissible limits than the other methods [15]. Adsorption method is a widely used for defluoridation, which depends on ions in fluid diffusing to the surface of a solid, where they bond with the solid surface or are held there by weak intermolecular forces. Among all of the defluoridation adsorbents, carbonaceous materials such as activated carbon [16] and carbon nanotubes [17] are the most commonly used adsorbents due to their large specific surface area, large quantity of surface functional groups, and abundant pore size distribution.

EG is an emerging member of carbon materials with porous structure, high surface area and presence of surface functional groups. It has drawn much scientific attention since its discovery due to its unique electronic and mechanical properties, excellent mobility of charge carriers. Moreover, mesoporous Al_2O_3/EG

composites was prepared to enhanced adsorption of Eu^{3+} [18]. It exhibits great promise for potential applications in adsorption for different substances such as methylene blue [19], oil [20] and Cr(VI) [21]. Moreover, EG has a good application as matrix because of its excellent property such as chemical inertness, stability under high temperature and corrosion resistance.

Recent studies revealed that some nano-sized metal oxides exhibit significant adsorption capacity and selectivity towards several toxic ions. The particles of alumina, ferric oxides, manganese oxides, magnesium oxides were classified as the promising adsorbents for toxic ions removal from aqueous systems [22–26]. It was further demonstrated that the alumina was exploited for the adsorption of anionic pollutants in aqueous solutions. And it has a great capacity for F^- adsorption [27–29]. Previous studies indicated that the nano-sized alumina which was impregnated to the surface of charcoals was found to be effective in the removal F^- [30]. The results suggested amorphous alumina was continually present in the charcoals and their particles was small size. At pH 7, optimum fluoride uptake by adsorbent that was calcined at 650 °C was observed. The fluoride uptake was 2.3 mg g^{-1} corresponding to a fluoride removal yield of 92% and a fluoride residual concentration of 0.76 mg L^{-1}. In the last research, the most important thing is not the lower adsorption capacity, but it is helpless to remove even trace amount of F^- in aqueous solutions.

In this work, an Al_2O_3/EG composite was easily and fast prepared to remove trace F^- in aqueous solutions, which combined the advantages of the large surface area of EG with the high F^- adsorption capacity of aluminum oxide. The experimental parameters for adsorption were optimized and the adsorption mechanism was elucidated by XRD, FSEM, EDS and FTIR.

2. Experimental section

2.1. Materials preparation

The Al_2O_3/EG nano-composites were synthesized with these steps. Firstly, a mixture of 25 mL $Al(NO_3)_3$ solution (0.25 mol/L) and 0.25 g EG was placed in a thermostatic bath at 30 °C for 120 min. Then, the solution mixture was dried at 100 °C for 8 h in a vacuum oven. Finally, the product was transferred in a muffle furnace with the temperature at 450 °C for 2 h, the obtained material was ground properly and homogenized. The as-synthesized material was subsequently used as absorbent.

2.2. Characterization

The crystalline phases of the samples were determined by XRD equipped with Cu Kα radiation (λ = 0.15406 nm). FSEM was used to analyze the morphology of the samples, where the composite particles were coated with gold and the images were then taken at 15.0 kV. The FTIR spectra were recorded in KBr pellets with a Bruker Vertex 70 instrument in a range between 400 and 4000 cm^{-1}.

2.3. Zeta potential measurement

The zeta potential of the surface of the Al_2O_3/EG composite was measured using a BDL-B surface potential (Malvern nano ZS90 Instruments, Britain).

2.4. Adsorption experiments

Batch adsorption experiments were performed in PVC conical flasks, each containing a 50 mL F^- solution. A stock F^- solution (1000 mg/L) was prepared by dissolving 0.2210 g reagent grade NaF in 100 mL of distilled water. Model F^- water used for adsorption experiments was prepared by diluting the stock solution with distilled water. The solution pH was adjusted to the desired value with 0.1 M HCl or 0.1 M NaOH. The effect of pH on F^- adsorption was investigated by adjusting the pH of the F^- solution (5 mg/L) to 2.0–11.0 in the presence of 0.2 g adsorbent. To determine the effect of the adsorbent dose on the removal of F^-, the different amounts (0.1–0.6 g) of the Al_2O_3/EG adsorbent were suspended in F^- solutions in which the initial F^- concentration was 5 mg/L at pH of 4.0, the suspensions were shaken in a controlled shaker (THZ-82) at 200 rpm at 30 °C for 120 min. Afterwards, Al_2O_3/EG were separated from the solution using filter paper, and the filtrate was analyzed for residual F^- concentration by using Ion Selective Electrode. Adsorption

kinetic and isotherm experiments were performed at 30, 40 and 50 °C to investigate the effect of contact time (0–150 min) and initial concentration (3–100 mg/L). The specific amount of F^- adsorbed was calculated by following expression:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{1}$$

where, q_t (mg/g) is the adsorbed amounts at equilibrium, C_o and C_t (mg/L) are the initial and equilibrium concentrations of F^-, respectively. V (L) is the volume of the solution and m (g) is the amount of adsorbent used to carry out the experiments. The effect of pH on removal of F^- was studied by adjusting the pH of the solution using 0.1 M HCl and 0.1 M NaOH.

3. Results and discussion

3.1. XRD analysis

Fig. 1 showed the XRD patterns of the calcined EG (a), Al_2O_3 (b) and Al_2O_3/EG composite (c). The typical diffraction peaks at 2θ = 26.8° and 54.7° were attributed to the matrix of the EG structure, which could be assigned to (0 0 2) and (2 1 1) (Fig. 1a). Through Fig. 1b there was no crystalline structure with diffraction peaks of alumina. According to this, alumina was identified as amorphous [31]. So in Fig. 1c, diffraction peaks of alumina cannot be found.

3.2. The morphology of Al_2O_3/EG

The FSEM images of EG and Al_2O_3/EG nano-composites were shown in Fig. 2. The surface of EG was relatively smooth, as shown in Fig. 2a. After EG was modified with Al_2O_3, it could be seen that Al_2O_3 nano-peas were uniformly deposited on the surface of EG, as shown in Fig. 2b. It was also observed that Al_2O_3 dispersed on the EG surface showing peas-like morphologies with a diameter of 10–30 nm, a length of 20–50 nm, the length-diameter ratio
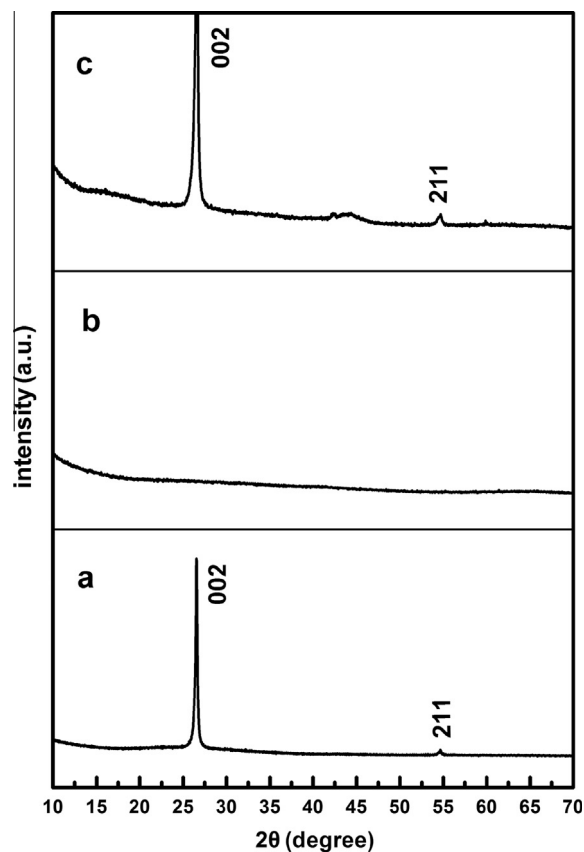

Fig. 1. XRD patterns of (a) EG, (b) Al_2O_3 and (c) Al_2O_3/EG.