Fluoride adsorption on modified natural siderite: Optimization and performance

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HIGHLIGHTS

- An optimum modified natural siderite (OMNS) was fabricated by the extrusion method.
- Calcination temperature and time and the mixing ratio were optimized to obtain OMNS.
- Oxidation of siderite to hematite attributed to high fluoride adsorption of OMNS.
- Solution pH had no significant effect on fluoride removal between 3.5 and 10.0.
- Fluoride adsorption on OMNS was reasonably spontaneous and endothermic.

ARTICLE INFO

ABSTRACT

Natural siderite modified by aluminum sulfate and aluminum sol was synthesized and characterized for F^- removal. Natural siderite powders, $Al_2(SO_4)_3$, and AlOOH were mixed with different ratios, granulated by an extrusion method, and calcined at different temperatures for different time durations. The optimum modified natural siderite (OMNS) was obtained with the mass ratio of 50 g:0.3 g:10 g for natural siderite powders:$Al_2(SO_4)_3$:AlOOH and calcinated at 450 °C for 3 h. Solution pH had no significant effect on F^- removal between 3.5 and 10.0. Kinetic results showed that adsorption followed the pseudo-second-order kinetic equation. Both the external adsorption and the intra-particle diffusion contributed to adsorption processes, while pore diffusion controlled fluoride adsorption on OMNS according to Bahangam equation. Thermodynamic data showed that fluoride adsorption on OMNS was reasonably spontaneous and endothermic. Moreover, fluoride adsorption was obviously constrained by the coexistence of HCO_3^- and PO_4^{3-}. Column studies revealed that breakthrough time and adsorption capacity were lower at higher concentration and/or higher flow rate. The XRD studies indicated the uptake of F^- by the OMNS attributed to the coexistence of hematite and γ-Al_2O_3 in the material.

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1. Introduction

It is well known that fluorine is an indispensable element for human healthy. Fluoride at a relative low level is beneficial in human body for the calcification of dental enamel and maintenance of healthy bones [1]. Thus, fluoride is *artificially* added to drinking water at approximately 1 mg L^{-1} to prevent dental decay [2]. However, excessive fluoride intake can result in dental and skeletal fluorosis and lesion of endocrine glands, thyroid, liver and other organs [3–5]. Groundwater is usually used as the source of drinking water in many countries. Groundwater with high fluoride concentration (>1.0 mg L^{-1}) as drinking water resources

is considered to be unsafe in China, where the drinking water guideline for F^- is 1.0 mg L^{-1} [6], although World Health Organization (WHO) has recommended the permissible limit of fluoride in drinking water is 1.5 mg L^{-1} [7]. High fluoride groundwater is widely distributed all over the world, including Tanzania, India, China, and Korea [8–10]. In China, for example, more than 30 million people are seriously affected by groundwater F^- [11]. Therefore, it is necessary to reduce fluoride concentration to acceptable level for high fluoride groundwater.

Various methods, such as ion-exchange, precipitation, adsorption and membrane processes, have been developed for defluoridation in groundwater [12–19]. Comparatively, adsorption has been received much attention due to its easily operation, low cost and being environmentally friendly process. A large number of adsorbents, including activated alumina [19], clay [20], zeolite [21], red mud [22], and synthetic oxide [23], have been studied for F^- removal. Among these adsorbents, activated alumina is widely

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used, since it is easily available and inexpensive [1,2]. However, the main disadvantage of activated alumina is low adsorption capacity at neutral pH and increased dissolved alumina in solution [24]. Moreover, many synthetic adsorbents with relatively good performance for fluoride adsorption are available only as fine powders that are difficult to separate from solution after adsorption. Recently, considerable work has been carried out to develop new adsorbents with high fluoride adsorption capacity and good mechanical strength. Natural siderite has been found to have good binding affinity for As in recent investigations [25,26]. As a cost-effective natural geomaterial, natural siderite has high reserves in China, up to around 2.0 billion kg, which would be the potential adsorbent material for removal of anions, like As species, from water solutions. However, very limited information is available for binding affinity of siderite for F^-.

In our previous study, Liu et al. have investigated F^- removal by synthetic siderite [6]. They found that the synthetic siderite has a good adsorption capacity for F^-, but is not cost-effective. Although the coarse grain size fractions of natural siderite (>0.50 mm) are ready to be directly used in fixed beds for water treatment, the fine grain size fractions, simultaneously generated in the process of mineral crushing, are not well utilized. To overcome these limitations, this study is to develop a novel adsorbent for defluoridation using natural siderite powder and aluminum chemicals, which have been considered to be a good scavenger for aqueous F^- [1,2]. Herein, aluminum sulfate is used to improve the fluoride adsorption capacity, and aluminum sol as a binder to enhance the granule mechanical strength as well as adsorption capacity.

Modified natural siderite has been developed by mixing, extrusion and calcination. Calcination temperature, calcination time, and the mixing ratio of natural siderite powder, $Al_2(SO_4)_3$, and AlOOH were optimized to obtain the optimum adsorbent for F^- removal. The optimum adsorbent was characterized by XRD and BET analysis. Adsorption characteristics for F^- removal on the adsorbent were evaluated with batch and column experiments.

2. Materials and methods

2.1. Adsorbent preparation

Natural siderite powders (NSPs) were sieved with a 150-mesh sieve. The sieved NSP, $Al_2(SO_4)_3 \cdot 18H_2O$, 25% AlOOH and deionized water were mixed with different mass ratio. The mixture was extruded to the strips, with a diameter of 2.0 mm, under a pressure of about 5.5 MPa [14]. The obtained strips were calcined at 300 °C, 350 °C, 400 °C, 450 °C and 475 °C for 0.5 h, 1 h, 2 h, 3 h, 4 h and 5 h in a muffle furnace, and then broken up manually into short granules with 3–4 mm length. The natural siderite modified at the optimum mixing ratio, calcination temperature and calcination time was referred as OMNS.

2.2. Batch experiments

A 1000 mg L^{-1} fluoride stock solution was prepared by dissolving 2.21 g NaF in 1 L of deionized water at room temperature. The test solution for this experiment was prepared by diluting the stock solution to certain concentrations. The pH value for test solution was adjusted by 0.1 M HCl and 0.1 M NaOH. All reagents used were of analytical grade.

Batch tests were performed in 100 mL high density polyethylene bottles using 0.50 g of adsorbents and 50 mL of fluoride solution. Fluoride concentration varied between 2 and 25 mg L^{-1}. Adsorption was conducted in a shaking water bath with a temperature controller, with a speed of 150 rpm. At desired time, the suspension was filtered through 0.45-μm membrane filters, and then analyzed for residual fluoride. All fluoride solutions were synthesized using deionized water.

2.3. Column study

Perspex columns with an inner diameter of 3 cm and height of 15 cm were used to evaluate adsorption performance of OMNS. The column was packed with OMNS, with the bed height of 12 cm. Feed water with desired fluoride concentration was prepared by deionized water and tap water, and flowed continuously from the bottom of the column to the top at desired flow rate using peristaltic pump. The effluent was sampled from the top of the column at regular time intervals and analyzed for F^-, Fe, and Al concentrations.

Column adsorption was first performed to treat F^--spiked tap water with the initial fluoride concentration of 3 mg L^{-1} and flow rate of 4 mL min^{-1}. Fluoride desorption from the F^--loaded OMNS was carried out with 0.1 M NaOH as eluent at the flow rate of 5 mL min^{-1}. The column effluents were collected at regular time intervals for fluoride determination. After desorption, OMNS was activated using 0.001 M HCl for 24 h at the flow rate of 1 mL min^{-1}, followed by washing with deionized water until the effluent pH was around 6.5.

2.4. Analysis

The X-ray diffraction patterns of NSP and OMNS were recorded by a D/MAX 2500 X-ray diffractometer (graphite monochromator, 2θ range 2.6–70°, step 0.01°, counting time 5 s per step), operated at 40 kV and 100 mA. The BET specific surface areas, total pore volume and mean pore diameter of the pristine NSP and OMNS were determined by using N_2 adsorption–desorption analysis. Prior to the nitrogen adsorption analysis, all the adsorbent samples were degassed at 200 °C for 1 h.

The pH$_{zpc}$ of OMNS was determined by *potentiometric* titration method. Titration was carried out using Metrohm automatic titrator (Metrohm, 905, Switzerland). Before titration, 0.2 g OMNS was separately added to 80 mL of KCl solution with concentration of 0.01 mol L^{-1}, 0.05 mol L^{-1} or 0.1 mol L^{-1}, and agitated for 24 h to reach equilibrium. The suspension was maintained at 25 °C, and continuously purged with high purity N_2 (99.99%). The suspension was titrated from pH 4 to pH 9. TIAMO 2.3 software was used to control and record the titration process.

Fluoride concentration was measured using a fluoride selective electrode (CHN090, Thermo Fisher Scientific, USA) by using total ionic strength adjustment buffer (TISAB) solution (142 g of $(CH_2)_6N_4$, 85 g of KNO_3 and 9.97 g of $C_6H_4Na_2O_8S_2 \cdot H_2O$ in 1000 mL) to eliminate the interference of coexisting anions. Prior to analysis, 20 mL solution was mixed with 10 mL TISAB and diluted to a final volume of 50 mL with deionized water. Concentrations of Fe and Al in solutions were analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-AES) (iCAP 6300, Thermo).

3. Results and discussion

3.1. The optimization of OMNS

An ideal adsorbent should possess high adsorption capacity and good mechanical strength. *In this study*, the calcination temperature, calcination time and the mixing ratio of NSP, $Al_2(SO_4)_3$ and AlOOH were optimized for F^- removal. Fluoride removal was evaluated by batch experiments with initial fluoride concentration of 5 mg L^{-1}, adsorbent dose of 10 g L^{-1}, and contact time of 24 h.