Fluoride adsorption on modified natural siderite: Optimization and performance

Yue Shan, Huaming Guo *  

a State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing 100083, PR China  
b School of Water Resources and Environment, China University of Geosciences, Beijing 100083, PR China

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

Article history:  
Received 23 November 2012  
Received in revised form 3 March 2013  
Accepted 6 March 2013  
Available online 13 March 2013

Keywords:  
Column experiments  
F  
Modification  
Regeneration  
Removal

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 Bahnagam 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 2 O 3 in the material.

© 2013 Elsevier B.V. All rights reserved.

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...
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 about 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, $\text{Al}_2(\text{SO}_4)_3$, and $\text{AlOOH}$ 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, $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$, 25% $\text{AlOOH}$ 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$_{pzc}$ 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$_3$)$_2$NH$_2$, 85 g of KNO$_3$ and 9.97 g of CsH$_2$Na$_2$O$_2$S$_2$H$_2$O 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 NSF, $\text{Al}_2(\text{SO}_4)_3$, and $\text{AlOOH}$ 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.
3.1.1. Effect of calcination temperature and calcination time

Calcination temperature and calcination time are major factors affecting F\(^{-}\) adsorption on granulated adsorbent. The sieved NSP were mixed with Al\(_2\)(SO\(_4\))\(_3\) and AIOOH, respectively, with a mass ratio of 125:1 in terms of Al\(^{3+}\). Then, the blends were extruded to the strips. The strips were calcined at different temperatures for different time period, which were used for fluoride adsorption.

Fluoride adsorption capacities are shown in Fig. 1. For Al\(_2\)(SO\(_4\))\(_3\)-modified NSP, the calcination time had little influence on fluoride adsorption on materials calcined at 300 °C and 350 °C (Fig. 1a). Fluoride adsorption on 300 °C-calcined adsorbents was 0.365 mg g\(^{-1}\), slightly higher than 0.345 mg g\(^{-1}\) on 350 °C-calcined adsorbents. For calcination temperatures of 400 °C and 450 °C, fluoride adsorption increased with increasing calcination time at first 3 h, and reached the maximum at 3 h, (0.468 mg g\(^{-1}\) and 0.457 mg g\(^{-1}\) respectively). After that, fluoride adsorption began to decrease to 0.459 mg g\(^{-1}\) and 0.403 mg g\(^{-1}\), respectively. It may indicate that at <350 °C adsorption sites are independent of calcinations time, while at >400 °C adsorption sites generally increased with calcinations time.

For AIOOH-modified NSP, fluoride adsorption capacities were almost constant with increasing calcination time at different calcination temperatures (Fig. 1b). Fluoride adsorption capacities increased in the following order: 400 °C < 475 °C < 350 °C < 450 °C. The optimal fluoride adsorption capacity was 0.376 mg g\(^{-1}\) at 450 °C. Fluoride adsorption was mainly due to the exchange between the surface metal hydroxide and fluoride. It is possible that calcinations at high temperature (>450 °C) may result in the decrease or loss of metal hydroxide, leading to low fluoride adsorption capacities [27]. Therefore, calcination at 450 °C for 3 h was selected for adsorbent modification in following experiments.

3.1.2. Effect of mixing ratio

The NSP, Al\(_2\)(SO\(_4\))\(_3\) and AIOOH were mixed with different mass ratios. The quantity of NSP (50 g) was fixed. The quantities of Al\(_2\)(SO\(_4\))\(_3\) varied between 0.2 and 3.0 g (as Al), and the quantities of AIOOH changed between 0.4 and 10 g (as Al). After extruded to strips, mixtures were calcined at 450 °C for 3 h. Fig. 2 shows the effect of the mixing ratios on fluoride adsorption. When the mass ratios of NSP to Al\(_2\)(SO\(_4\))\(_3\) (as Al) were 50:0.2 and 50:0.3, fluoride adsorption obviously increased with increasing AIOOH dosage, and reached the maximum at 0.402 mg g\(^{-1}\) and 0.489 mg g\(^{-1}\) for NSP:Al\(_2\)(SO\(_4\))\(_3\) (as Al):AIOOH (as Al) of 50:0.2:10 and 50:0.3:10, respectively. As the ratio of NSP:Al\(_2\)(SO\(_4\))\(_3\) (as Al):AIOOH (as Al) changed from 50:1.8:0.4 to 50:1.8:1.0, fluoride adsorption showed no significant variation (0.47–0.49 mg g\(^{-1}\)). Moreover, the increasing dosage of AIOOH had little effect on fluoride adsorption at NSP:Al\(_2\)(SO\(_4\))\(_3\) (as Al) ratio of 50:2.4 and 50:3.0 (0.493 mg g\(^{-1}\) and 0.497 mg g\(^{-1}\), respectively). Except for these adsorbents with the NSP:Al\(_2\)(SO\(_4\))\(_3\) (as Al) ratios of 50:0.2 and 50:0.3, other released high Fe and Al concentrations in solution during fluoride adsorption. Therefore, the NSP:Al\(_2\)(SO\(_4\))\(_3\):AIOOH ratio of 50:0.3:10 was selected as the optimum mixing ratio for following experiments.

3.2. Characterization of OMNS

The OMNS adsorbents with 2 mm in diameter and 3–4 mm in length are shown in Fig. 3. The XRD patterns of pristine NSP and...
OMNS are given in Fig. 4. The mineral components of two samples are mainly siderite, hematite, kaolinite and quartz. It was observed that at $2\theta = 24.7^\circ$, $32.0^\circ$ and $42.8^\circ$ the diffraction peak intensity of OMNS for siderite was weaker after modification and the relative content of siderite decreased from 85.6% to 45.3% relative to NSP. The diffraction peak intensity of modified siderite was stronger than that of the pristine at $2\theta = 26.6^\circ$ and $35.7^\circ$ for hematite. The relative content of hematite increased from <1.0% to 39.5%. This indicated that siderite was partly oxidized into hematite, which was attributed to F$^-_{\text{removal}}$.

Moreover, at $2\theta = 33.2^\circ$ the appearance of crystal peaks attributed to the formation of both hematite and $\gamma$-$\text{Al}_2\text{O}_3$, indicating siderite and aluminum chemicals were converted to hematite and $\gamma$-$\text{Al}_2\text{O}_3$ during the calcination, respectively. At $2\theta = 19.4^\circ$ the diffraction peak intensity of $\gamma$-$\text{Al}_2\text{O}_3$ was very weak. However, the diffraction peak of $\gamma$-$\text{Al}_2\text{O}_3$ was not obvious at $2\theta = 37.6^\circ$, $39.5^\circ$, $45.8^\circ$ and $67.0^\circ$, which indicated the limited amount of $\gamma$-$\text{Al}_2\text{O}_3$ in the material. The formation of $\gamma$-$\text{Al}_2\text{O}_3$ after modification could enhance the fluoride adsorption.

The $N_2$ adsorption and desorption isotherms of two adsorbents are plotted in Fig. 5. OMNS had two adsorbents had desorption hysteresis phenomenon, suggesting the mesoporous nature of the adsorbents [2]. The BET specific surface area of OMNS was 79.52 m$^2$/g, greater than that of the pristine NSP (51.70 m$^2$/g). The total pore volume of OMNS (0.0708 mL/g) was two times larger than that of the pristine NSP. It indicated that NSP had great active sites for fluoride adsorption after modification. The mean pore diameters of the pristine NSP and OMNS were 5.48 nm and 7.56 nm, respectively.

3.3. Batch experiments

3.3.1. Effect of pH

Adsorption of ions on the oxide surface is generally affected by pH of aqueous solutions. Therefore, effect of initial solution pH on F$^-_{\text{removal}}$ by OMNS was studied in the pH range of 2–12. Fig. 6 shows the effect of the initial solution pH (pHi) on fluoride adsorption. At pH <3.5 and >10, fluoride adsorption greatly decreased to 0.153 and 0.025 mg g$^{-1}$, respectively. However, pH between 3.5 and 10 had no significant effect on fluoride adsorption, and fluoride adsorption capacity remained almost constant (0.451–0.475 mg g$^{-1}$). The final solution pH after adsorption (pHf) was around 7.8 for the initial pH range between 3.5 and 10. It was demonstrated that OMNS had a significant capacity in maintaining the adsorption system at near neutral pH during the experiments, which may be the main reason that OMNS could keep a relatively constant fluoride adsorption.

In the initial solution pH range between 3.5 and 6.8, the positive OMNS surface adsorbed negatively charged fluoride with the electrostatic attraction [5], since the pHzpc of the material was around $6.8 \pm 0.2$. At the neutral and alkaline pH range (pH = 6.8–10), ligand exchange between F$^-$ and hydroxyl groups may occur [5]. However, the sharp decrease in fluoride adsorption on OMNS at acidic pH < 3.5 possibly attributed to the formation of weak hydrofluoric.
The decrease in fluoride adsorption in the alkaline pH range (pH > 10) may be due to the competition of the hydroxyl ions with F\(^-\) for surface sites on OMNS or electrostatic repulsion of F\(^-\) to the negatively charged OMNS surface.

3.3.2. Kinetic study

Adsorption kinetic study was carried out with initial fluoride concentration of 5 mg L\(^{-1}\) and adsorbent dose of 10 g L\(^{-1}\) at 25 °C. Pseudo-first-order adsorption model, pseudo-second-order adsorption model and intraparticle diffusion model were used to test kinetic data to investigate the mechanisms of adsorption. Those models were shown in Eqs. (1)–(3), respectively [28–30].

\[
\log(q_t - q_e) = \log q_{eq} - \frac{k_1}{2.303} t
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_{eq}} + \frac{1}{q_{eq}} t
\]

\[
q_t = \frac{q_{eq} b C_0}{(1 + b C_0 t)}
\]

where \(q_t\) is the adsorption amount at time \(t\) (mg g\(^{-1}\)); \(q_{eq}\) is the adsorption amount at equilibrium (mg g\(^{-1}\)) in the pseudo-first-order adsorption model; \(k_1\) is the rate constant of pseudo-first order adsorption reaction (min\(^{-1}\)); \(q_{eq}\) is the adsorption amount at equilibrium (mg g\(^{-1}\)) in the pseudo-second-order adsorption model; \(k_2\) is the rate constant of pseudo-second order adsorption reaction (g mg\(^{-1}\) min\(^{-1}\)); \(k_3\) is the intra-particle diffusion rate constant (mg g\(^{-1}\) min\(^{-0.5}\)).

The kinetic parameters estimated are shown in Table 1. It was found that the correlation coefficient \((R^2 = 0.995)\) of the pseudo-second-order model is higher than that \((R^2 = 0.988)\) of the pseudo-first-order model. The modeled \(q_{eq}\) value (0.530 mg g\(^{-1}\)) in the pseudo-second-order model is consistent with the experimental value \(q_e\) (0.475 mg g\(^{-1}\)). It indicated that the kinetic data fitted the pseudo-second-order adsorption rate model better than the pseudo-first-order adsorption rate model.

The plot of intra-particle diffusion is shown in Fig. 7a. The plot reflected a three-stage nature, with an initial linear portion followed by an intermediate linear portion and a plateau. The initial curve of the plot was due to the diffusion of F\(^-\) through the solution to the external surface of OMNS or the boundary layer diffusion. The second linear portion of curves described the intraparticle diffusion of F\(^-\) on OMNS surface, and the last portion was the adsorption equilibrium stage [31,32]. It was observed that the second portion did not pass through the origin, indicating that the adsorption mechanism on OMNS was complex and both the external adsorption and intra-particle diffusion contributed to the adsorption process [33].

The data were further analyzed to evaluate the slow step occurring in the adsorption system using Bahangam’s equation (Eq. (4)) [31].

\[
\log \log \left( \frac{C_0}{C_0 - q_m} \right) = \log \left( \frac{k_0 m}{2.303 V} \right) + \alpha \log t
\]

where \(C_0\) is the initial F\(^-\) concentration in solution (mg L\(^{-1}\)); \(V\) is the volume of the solution (mL); \(m\) is the weight of OMNS (adsorbent) used per liter of solution (g L\(^{-1}\)); \(q\) (mg g\(^{-1}\)) is the amount of F\(^-\) retained in the adsorbent at time \(t\) (min); and \(\alpha\) (<1) and \(k_0\) are constants of the system examined. The values of \(\alpha\) and \(k_0\) can be calculated by calculating \(\log \log \left(\frac{C_0}{C_0 - q_m}\right)\) against \(\log t\) (Fig. 7b). The plot was found to be linear, indicating that the kinetics conformed to Bahangam equation, and fluoride adsorption on OMNS was pore-diffusion controlled [31].

3.3.3. Adsorption isotherm

The isotherm experiments were carried out with the initial fluoride concentrations between 2 and 25 mg L\(^{-1}\) at 15–45 °C. It was found that absorbed F\(^-\) increased with increasing initial fluoride concentration. For example, adsorption of F\(^-\) increased from 0.189 to 2.276 mg g\(^{-1}\) with an increase in initial fluoride concentration from 2 to 25 mg L\(^{-1}\) at 25 °C. This may be due to the high concentration gradient (driving force) at high initial fluoride concentration [2]. However, the removal efficiency decreased due to the finite active sites, resulting in the relatively lower efficiency at the higher initial concentration [34].

The experimental data were fitted to Langmuir and Freundlich isotherm models based on non-linear regression, which are expressed as Eqs. (5) and (6), respectively.

\[
q_{eq} = \frac{q_m b C_0}{(1 + b C_0)}
\]

\[
q_{eq} = K_s C_0^{1/n}
\]
where \( C_e \) is the equilibrium F\(^{-}\) concentration (mg L\(^{-1}\)); \( q_{ae} \) is the Langmuir adsorption capacity (mg g\(^{-1}\)); \( q_m \) is the Freundlich equilibrium adsorption capacity (mg g\(^{-1}\)); \( q_n \) is the maximum monolayer adsorption capacity (mg g\(^{-1}\)); \( b \) is the equilibrium adsorption constant (L mg\(^{-1}\)); \( K_p \) and \( n \) are the empirical constants being dependent of several environmental factors.

The plots of Langmuir and Freundlich isotherms are presented in Fig. 8. The isotherm constants are shown in Table 2. The applicability of the isotherms was compared by evaluating the correlation coefficients \( R^2 \), showing that the data fitted the Langmuir and the Freundlich models well with correlation coefficients 0.982–0.996 and 0.954–0.996, respectively. Adsorption capacity, \( q_m \) (mg g\(^{-1}\)), increased with increasing reaction temperature. It indicated that the OMNS surface has good affinity for the F\(^{-}\), and the adsorption process is endothermic in nature. The \( q_m \) obtained was 5.460 mg g\(^{-1}\) at 45°C. The Freundlich constants of \( n \) (1.342–1.536) lying in the range 1–10 confirmed the favorable conditions of adsorption on OMNS, allowing for multilayer adsorption.

3.3.4. Thermodynamic study

Thermodynamic parameters, such as standard free energy change (\( \Delta G^0 \)), standard enthalpy change (\( \Delta H^0 \)) and standard entropy change (\( \Delta S^0 \)) are described as Eqs. (7)–(9) [35,36].

\[
\Delta G^0 = -RT\ln K_c
\]

\[
K_c = \frac{C_{ae}}{C_r}
\]

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\]

where \( \Delta G^0 \) is free energy change (kJ mol\(^{-1}\)); \( R \) is universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)); \( T \) is absolute temperature (K); \( K_c \) is the adsorption equilibrium constant; \( C_{ae} \) is the equilibrium concentration on the adsorbent (mg L\(^{-1}\)); \( C_r \) is the equilibrium concentration in solution (mg L\(^{-1}\)); \( \Delta H^0 \) is enthalpy change (kJ mol\(^{-1}\)); \( \Delta S^0 \) is entropy change (kJ mol\(^{-1}\) K\(^{-1}\)).

The values of \( \Delta G^0 \), \( \Delta H^0 \) and \( \Delta S^0 \) are summarized in Table 3. It shows that \( \Delta G^0 \) is negative, which indicated that adsorption of F\(^{-}\) on OMNS was a spontaneous process. The positive value of \( \Delta H^0 \) for the reaction indicated the endothermic nature of the reaction. Therefore, increasing reaction temperature promoted fluoride adsorption. The value of \( \Delta S^0 \) is also positive, which suggested the increased randomness at the solid/solution interface during fluoride adsorption.

3.3.5. Effect of coexisting anions

High fluoride groundwater contained other anions that may affect fluoride adsorption. Therefore, it is necessary to study effects of coexisting anions, including Cl\(^{-}\), SO\(_4^{2-}\), NO\(_3^-\), HCO\(_3^-\) and PO\(_4^{3-}\), on fluoride adsorption.

Fig. 9 showed that the presence of Cl\(^{-}\), SO\(_4^{2-}\) and NO\(_3^-\) had no significant effect on F\(^{-}\) removal even at a concentration of 800 mg L\(^{-1}\), probably due to the fact that the interaction of Cl\(^{-}\), SO\(_4^{2-}\) and NO\(_3^-\) with OMNS was weak [38]. However, the presence of HCO\(_3^-\) showed negative effect at concentrations >200 mg L\(^{-1}\). At HCO\(_3^-\) concentration of 800 mg L\(^{-1}\), fluoride adsorption capacity was 0.336 mg g\(^{-1}\). The coexistence of phosphate significantly depressed fluoride adsorption on OMNS. Fluoride adsorption decreased from 0.475 to 0.145 mg g\(^{-1}\) when PO\(_4^{3-}\) concentration increased from 0 to 800 mg L\(^{-1}\).

The reduction in fluoride adsorption observed in the coexistence of HCO\(_3^-\) and PO\(_4^{3-}\) not only resulted from the competition between F\(^{-}\) and these anions for active adsorption sites, but also the high affinity for HCO\(_3^-\) and PO\(_4^{3-}\) on OMNS. Moreover, the higher concentrations of coexisting anions occupied more active sites, resulting in more powerful competitive adsorption and lower adsorption capacity for F\(^{-}\). Similar results were obtained for adsorption of F\(^{-}\) from the aqueous solution using ceramic adsorbent and synthetic siderite [6,37].

Table 1

| Kinetic parameters for fluoride adsorption on OMNS (initial fluoride of 5 mg L\(^{-1}\), adsorbent dose of 10 g L\(^{-1}\), contact time = 10–780 min, T = 25°C). |
|---|---|---|---|---|---|
| \( q \) (mg g\(^{-1}\)) | Pseudo-first-order | | Pseudo-second-order | | Intra-particle diffusion | Bahangam’s equation |
| \( r^2 \) | \( K \) (min) | \( q \) (mg g\(^{-1}\)) | \( r^2 \) | \( K_c \) (g mg\(^{-1}\) min\(^{-1}\)) | \( q \) (mg g\(^{-1}\)) | \( r^2 \) | \( K_c \) (g mg\(^{-1}\) min\(^{-1}\)) | \( r^2 \) | \( v \) | \( k_a \) |
| 0.475 | 0.988 | 0.261 | 0.388 | 0.995 | 0.945 | 0.530 | 0.970 | 0.0175 | 0.991 | 0.708 | 0.120 |

Fig. 7. Plot of intraparticle diffusion model (a) and Bahangam’s equation (b) (initial fluoride of 5 mg L\(^{-1}\), adsorbent dose of 10 g L\(^{-1}\), contact time of 10–780 min, T = 25°C).
3.4. Column experiment

3.4.1. Effect of initial fluoride concentration

Tap water and deionized water were used to synthesize fluoride solution. The major components of tap water are shown in Table 4. Fig. 10 showed the breakthrough curves of OMNS-packed columns for F\(^{-}/\)C\(_{0}\)-spiked deionized water and tap water. The breakthrough point for the columns was set at 1.0 mg L\(^{-1}\)F\(^{-}/\)C\(_{0}\) in the effluents according to the Chinese drinking water standards. Fluoride removal by the column was investigated with initial fluoride concentrations between 3 and 5 mg L\(^{-1}\) at a flow rate of 1.8 mL min\(^{-1}\). The pore volumes (PVs) at the breakthrough point were 2092 (accumulated adsorption capacity of 5.97 mg g\(^{-1}\)) and 824 (accumulated adsorption capacity of 4.02 mg g\(^{-1}\)) for initial fluoride concentrations of 3 and 5 mg L\(^{-1}\), respectively, in terms of F\(^{-}/\)C\(_{0}\)-spiked deionized water. For F\(^{-}/\)C\(_{0}\)-spiked tap water, PV at the breakthrough point were 647 (accumulated adsorption capacity of 1.55 mg g\(^{-1}\)) and 345 (accumulated adsorption capacity of 1.48 mg g\(^{-1}\)) for initial fluoride concentrations of 3 and 5 mg L\(^{-1}\), respectively. With the higher initial fluoride concentration, the breakthrough curve was sharper, showing that the columns got saturated more quickly with the higher initial fluoride concentration in feedwater\(^{-38,32}\). The pH of F\(^{-}/\)C\(_{0}\)-spiked tap water was 7.6 ± 0.2, which is higher than pHzpc of OMNS. Therefore, the lower adsorption capacity for F\(^{-}/\)C\(_{0}\)-spiked tap water than F\(^{-}/\)C\(_{0}\)-spiked deionized water possibly attributed to coulombic repulsion between the negative charge on the surface and F\(^{-}\) in solution\(^{-24}\), and competitive adsorption with the coexisting anions occurring in tap water (such as HCO\(_{3}\), Cl\(^{-}\), NO\(_{3}\), and SO\(_{4}\)^{2-}). Concentrations of Fe and Al in effluents met the Chinese Drinking Water Standards, indicating that this adsorbent was suitable for filter application.

Table 2

<table>
<thead>
<tr>
<th>(T (\degree C))</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(R^2)</td>
<td>(q_{m} \text{ (mg g}^{-1}))</td>
</tr>
<tr>
<td>15</td>
<td>0.982</td>
<td>3.680</td>
</tr>
<tr>
<td>25</td>
<td>0.988</td>
<td>4.423</td>
</tr>
<tr>
<td>35</td>
<td>0.991</td>
<td>4.975</td>
</tr>
<tr>
<td>45</td>
<td>0.996</td>
<td>5.460</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>(C_0 \text{ (mg L}^{-1})</th>
<th>(\Delta H^0 \text{ (kJ mol}^{-1})</th>
<th>(\Delta S^0 \text{ (kJ mol}^{-1} \text{ k}^{-1})</th>
<th>(\Delta G^0 \text{ (kJ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 \degree C</td>
<td>25 \degree C</td>
<td>35 \degree C</td>
</tr>
<tr>
<td>2</td>
<td>13.604</td>
<td>0.0683</td>
<td>-4.498</td>
</tr>
<tr>
<td>5</td>
<td>25.959</td>
<td>0.1080</td>
<td>-5.318</td>
</tr>
<tr>
<td>10</td>
<td>21.944</td>
<td>0.0945</td>
<td>-5.237</td>
</tr>
<tr>
<td>15</td>
<td>19.297</td>
<td>0.0857</td>
<td>-4.502</td>
</tr>
<tr>
<td>20</td>
<td>19.548</td>
<td>0.0837</td>
<td>-4.581</td>
</tr>
<tr>
<td>25</td>
<td>26.662</td>
<td>0.1059</td>
<td>-3.682</td>
</tr>
</tbody>
</table>

Fig. 8. Isotherms plots for F\(^{-}\) adsorption on OMNS at 15 \degree C (a), 25 \degree C (b), 35 \degree C (c), 45 \degree C (d) (initial fluoride concentration: 2–25 mg L\(^{-1}\), adsorbent dose of 10 g L\(^{-1}\), contact time = 780 min).
3.4.2. Effect of empty bed contact time

Empty bed contact time (EBCT) determines the residence time during which the solution being treated is in contact with the adsorbent. Therefore, EBCT may strongly affect adsorption, especially if the adsorption mainly depends on the contact time between the adsorbent and adsorbate [26,39].

Effect of flow rate was studied with a fixed initial fluoride concentration of 3 mg L\(^{-1}\), corresponding to EBCT of 47, 21 and 14 min, respectively. The breakthrough curves are shown in Fig. 11. It was found that, as EBCT decreased, the breakthrough curve became sharper. Subsequently, the breakthrough time and adsorption capacity decreased. It was observed that with an increase in flow rate from 1.8 to 6 mL min\(^{-1}\), breakthrough capacity decreased from 1.55 to 0.97 mg g\(^{-1}\). At the lower flow rate, interaction between adsorbent and adsorbate was more sufficient, resulting in a higher adsorption [32]. When the flow rate increased, the lower residence time resulted in lower column utilization. Therefore, the breakthrough time and the adsorption capacity decreased with increasing the flow rate [39].

3.4.3. Regeneration

Regeneration of the adsorbent may avoid environmental pollution of disposing the used adsorbents. Fluoride-loaded OMNS was used for in situ regeneration in the column which was broken through by F\(^-\)-spiked tap water with initial fluoride concentration of 3 mg L\(^{-1}\) at the flow rate of 4 mL min\(^{-1}\). Desorption of F\(^-\) was made with 0.1 M NaOH as eluent. It was found that 83% of retained
fluoride was eluted with 0.1 M NaOH solution at the flow rate of 5 mL min⁻¹. After desorption, OMNS was activated using 0.001 M HCl for 24 h at the flow rate of 1.0 mL min⁻¹, followed by washing with deionized water until the elution pH was around 6.5. Fig. 12 shows the breakthrough curve of fresh and regenerated adsorbent in one cycle. From Fig. 12, it was observed that the regenerated adsorbent had lower adsorption capacity as compared to fresh OMNS. Thus, the regeneration of the adsorbent required further investigations.

4. Conclusions
A granular aluminum chemical-modified natural siderite was synthesized for F⁻ removal by an extrusion method. The optimum modified natural siderite (OMNS) for fluoride adsorption was made by mixing NSP, Al₂(SO₄)₃ (as Al) and AIOOH (as Al) with the mass ratio of 50:0.3:10, and calcining the mixture at 450 °C for 3 h. Solution pH had no significant effect on F⁻ removal between 3.5 and 10.0. Kinetic data were well fitted to the pseudo-second order kinetic model. The adsorption process was controlled by both the external adsorption and the intra-particle diffusion. It showed that pore diffusion controlled fluoride adsorption on OMNS. Fluoride adsorption followed Freundlich isotherm model better than Langmuir isotherm model. The maximum static adsorption capacity was 4.42 mg g⁻¹ at 25 °C. With the coexistence of HCO₃⁻ and PO₄³⁻, fluoride adsorption was negatively affected. The breakthrough of OMNS-packets columns was dependent of the initial fluoride concentration and empty bed contact time. The sharper breakthrough curves were obtained at higher inlet fluoride concentration. As the flow rate increased, the breakthrough time and fluoride adsorption decreased. The OMNS had higher specific surface area, with larger pore volume and mean pore diameter than the NSP. The XRD pattern showed that the formation of hematite from siderite and γ-Fe₂O₃ from aluminum chemicals during modification attributed to high fluoride adsorption. The regenerated OMNS showed lower fluoride adsorption performance than the fresh one. The optimization of regeneration processes needs further investigations.

Acknowledgements
The study has been financially supported by the National Basic Research Program of China (the 973 program, No. 2010CB428804), the Natural Science Foundation of China (Nos. 41172224 and 41222020), and the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China (No. 708012).

References

Y. Shan, H. Guo / Chemical Engineering Journal 223 (2013) 183–191