

Removal of fluoride ion from groundwater by adsorption on lanthanum and aluminum loaded clay adsorbent

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Abstract A novel fluoride ion adsorbent, which uses natural clay modified by lanthanum and aluminum, was successfully prepared. The adsorbent was characterized by scanning electron microscope, BET surface area measurement, and X-ray photoelectron spectroscopy. Batch experiments were carried out to investigate the adsorbent performance for fluoride ion. Fluoride ion adsorbent onto modified clay followed the pseudo-second order kinetic model with the correlation coefficient value of 0.9846. The isotherm data was well fitted to the Langmuir model. The adsorption capacity of the modified clay was 1.3033 mg/g. The optimum pH value for fluoride ion removal was 6. The modified clay adsorbent can be regenerated by $KAl(SO_4)_2 \cdot 12H_2O$. Six times' regeneration experiments showed that the regeneration rate of the modified clay still higher than 80 %, and the mass loss rate lower than 10 %. The modified clay performed strong adsorption capacity for fluoride ion and high regeneration rate. It could be a cost-effective adsorbent to remove fluoride from groundwater in undeveloped regions.

Keywords Fluoride ion removal · Adsorption isotherms · Kinetics · Modified clay · Groundwater

Introduction

Groundwater is an important water resource in arid and semi-arid regions. People who consumes groundwater in excess of fluoride ion cause to bone diseases, including mottling of teeth and lesions of the endocrine glands, thyroid, liver and other organs (Tang et al. 2009; Umlong et al. 2012). As a result, the World Health Organization has set the standard for allowable fluoride ion concentration in drinking water to be 1.5 mg/L (WHO 2006).

Generally geochemical reactions in the sub-surface, water–mineral interaction, seemed to be the main cause of high concentration of fluoride ion in the groundwater which makes the process of defluoridation in natural condition difficult (Saxena and Ahmed 2001). Many defluoridation technologies have been studied, such as electro coagulation (Zhu et al. 2007), chemical precipitation (Mourabet et al. 2012), adsorption (Wang et al. 2009), ion exchange (Meenakshi and Viswanathan 2007), and membrane technology (Islam and Patel 2007). Above all, the adsorption technique has been approved as an effective and simple method for fluoride ion removal treatment (Mourabet et al. 2012). It has been found to be superior to the other techniques in terms of initial cost, flexibility and simplicity of design and ease of operation. Therefore, adsorption is becoming more appropriate in various studies (Arora et al. 2004; Li et al. 2011).

Accordingly, various adsorptive natural materials such as quicklime (Islam and Patel 2007), kaolinites (Meenakshi et al. 2008), red mud (Tor et al. 2009), and hydroxyapatite (Jiménez-Reyes and Solache-Ríos 2010) have been

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investigated as adsorbents to remove fluoride ion from water. However, compared to chemical materials, the fluoride removal efficiency of these natural materials has been evaluated lower. Though activated alumina possesses efficient defluoridation ability, the high cost of the preparation still limited the use in groundwater remediation (Ghorai and Pant 2005). Therefore, many modified natural materials such as activated carbon (Li et al. 2003; Sivasamy et al. 2001), activated kaolinites (Meenakshi et al. 2008), thermally treated quick lime (Islam and Patel 2007), granular red mud (Tor et al. 2009), and low cost clay (Zhang et al. 2009; Tor 2006) have been recommended. But for these modified natural materials, there was a problem concerns on the low adsorption capacity. Therefore, it is imperative to develop a new adsorbent for fluoride ion with a reasonable price and high capacity in order to widely use in poorly developed regions.

In general, adsorption mechanism could be physical or chemical adsorption, depending on the physical and chemical structural properties of the adsorbent. Physical adsorption mainly relies on active pore volume and specific surface area, and chemical adsorption depends more on chemical or electrical affinity (Morgan-Sagastume and Noyola 2008; Huo et al. 2011). Recently, researchers have been reported that the rare earth elements such as La^{3+} (Alemayehu and Lennartz 2009, 2010) and Ce^{3+} (Wang et al. 2013), which due to high electrical affinity to electronegative fluoride ion, could be the potential modified materials to synthesize new fluoride ion adsorbents. However, the high valuable price and the low optimum adsorption pH value of rare earth elements restricted their applications in the fluoride removal from groundwater. Therefore, it is necessary to develop a fluoride adsorbent with inexpensive price and high fluoride adsorption capacity at higher pH value operations (Wu et al. 2007). Under this circumstances, rare earth elements combining cheaper metal elements such as Fe^{3+} (Zhao et al. 2008) and Al^{3+} (Gong et al. 2012) on the framework supported low cost clay would be an appropriate and attractive way to prepare a fluoride adsorbent with the reasonable price and high adsorption capacity.

In this study, a fluoride adsorbent was synthesized by utilizing the natural clay with La^{3+} and Al^{3+} modification. The objectives of this work were to characterize the adsorbent and to evaluate its adsorption behavior. The effects of pH on the adsorption of fluoride ion and the adsorbent cycle stability were also investigated.

Description of field site

The field site is located in the southwest of Ningxia, China with an area of 3144 km². Geological formations of the site have been severely eroded, with remains of Proterozoic,

Cretaceous, Tertiary and Quaternary formations. It can be seen from Fig. 1a that the widely distributed Tertiary formations have well developed in the middle and southern part beneath the Quaternary formations. The Lower Cretaceous formation, which consists of severely weathered feldspar sandstone, has exposed in the northern part broadly. A generally spread compact clayey soil between the Tertiary and Quaternary formations caused the existence of Tertiary confined aquifer (Fu et al. 2014). This compact clayey soil has covered 70 % of the study site with the thickness variation between 200 and 400 m from the northern part to the southern. A developed blind fault of the Cretaceous and the Tertiary formation led the Tertiary confined aquifer to be recharged with a high hydraulic head pressure. Overall, three types of aquifer including Cretaceous unconfined aquifer, Tertiary confined aquifer and Quaternary pore aquifers have constituted the general aquifer. Above all, the Tertiary confined aquifer has been the target layer containing the main groundwater source of the study site. The groundwater flow of the target layer is from north to south. The groundwater is recharged through the Cretaceous and Tertiary blind fault, and groundwater discharges to the adjacent regions and artificial abstraction. It can be seen from the Fig. 1b that the concentration of fluoride ion in the target layer increases along with the groundwater flow. According to the results of groundwater sampling, a great number of fluoride ion concentrations have exceeded the Chinese drinking water standard of 1.0 mg/L. Moreover, the sampling of fluoride ion concentration more than 2.0 mg/L is presented in a line which from SuPu, XingPing to JiangTai. The highest concentration of fluoride ion measured for XiTan is 2.8 mg/L.

Materials and methods

Materials

The clay used in this study was obtained from Xiji, Ningxia province, China. Deionized (DI) water was used throughout the experiments. Stock fluoride ion solution of 1000 mg/L was prepared from dried sodium fluoride. The solutions of required concentrations were prepared by diluting the stock solution. All chemical reagents were analytical grade. NaF (99 %), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99 %), $\text{Al}_2(\text{SO}_4)_3$ (99 %), NaOH (99 %), HCl (36 %), HNO_3 (65 %) and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (99 %) were obtained from Chemical Engineering Company of Beijing, China.

Synthesis of modified clay

Clay material was washed twice with DI water and dried at 50 °C for 2 h. Dried caly (1.00 g) mixed with 0.22 mol/L

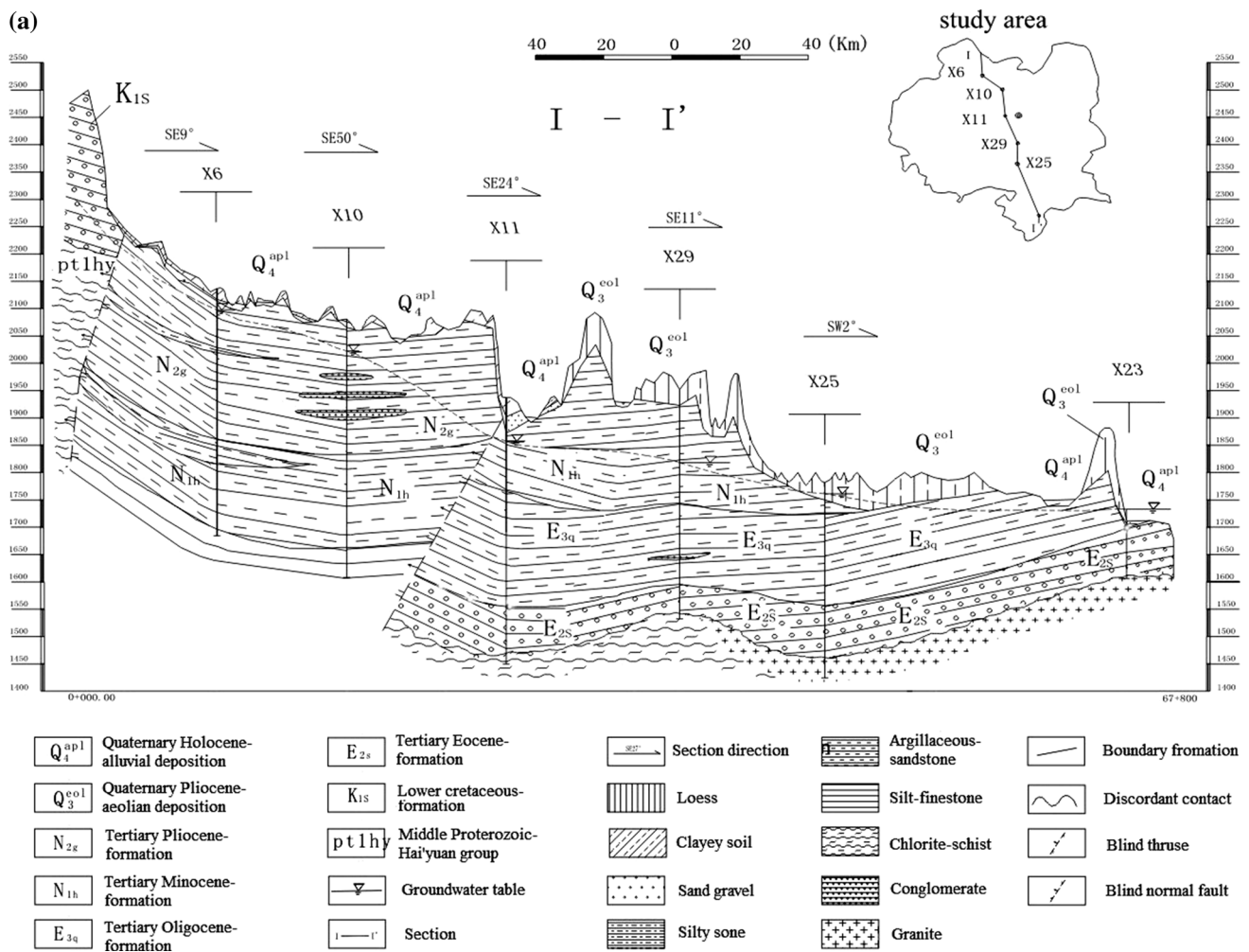


Fig. 1 The hydrogeological cross section of Xiji, Ningxia province, China (a) and the fluoride ion distribution at this field site (b)

Al(OH)₃ (1.5 mL) and 0.004 mol/L La(NO)₃·6H₂O (2.0 mL) into a beaker with 50 mL DI water stirred at 200 rpm. After 10 h, the modified clay was dried at 90 °C for 2 h in an oven and then thermally treated at 300 °C for 2 h in the furnace. Finally, Modified clay was washed with DI water to neutral pH, and the prepared adsorbent was stored in a polyethylene bottle for the following experiment.

Characterization of modified clay

A high qualitatively scanning electron microscope (SEM) (JEOL Ltd., Japan) was used to examine the surface morphology of raw clay and modified clay. The elemental composition of raw clay and modified clay were determined by energy dispersive X-ray analysis. Surface areas of both raw clay and modified clay were measured by nitrogen chemisorptions measurements with BET analysis

(SSA-3200C, Builder Electronic Technology Co., Ltd., China). The binding energies and atom ratios of the elements of modified clay before and after adsorption were obtained by using X-ray photoelectron spectroscopy (XPS) (Thermo Corporation, USA). A conventional Al Kα anode radiation source was used as the excitation source. The binding energies were calibrated by the C1s binding energy at 284.8 eV. XPS data processing and peak fitting were performed using a nonlinear least-squares fitting program.

Adsorption experiments

Fluoride ion solution (50 mL) was added to a 100 mL polyethylene bottle with the concentration of 4.89 mg/L. The modified clay (1.00 g) was added to a polyethylene bottle and shaken in incubator shaker at 200 rpm. At each time of 60, 120, 240, 360, 480, 600, 720, 840, 960 and 1080 min, the solution was collected and filtered with

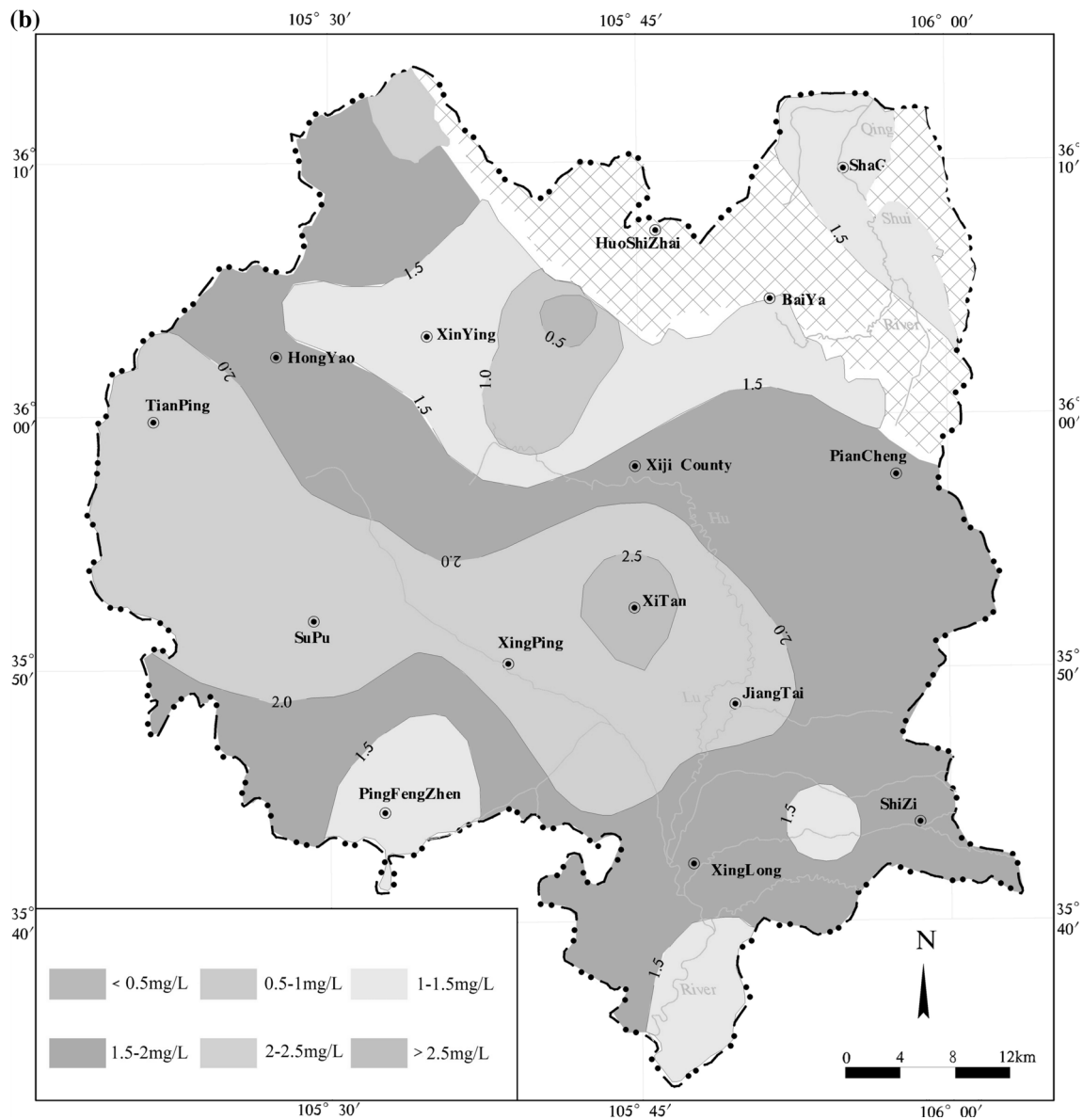


Fig. 1 continued

0.45 μm membrane for analysis, respectively. Residual fluoride ion was analyzed by a fluoride selective electrode (Weiye Instruments, Shanghai, China) and the amount of fluoride adsorbed was calculated by the following equation:

$$q_e = (C_0 - C_e) \times \frac{V}{W} \tag{1}$$

where q_e is the adsorption capacity (mg/g) at equilibrium, C_0 and C_e are the initial and equilibrium fluoride concentrations (mg/L), respectively; V is the volume (mL) of solution and W is the mass (g) of modified clay used. Experiments were conducted in duplicates, and the mean values were plotted.

In the batch adsorption experiments, the factors of connecting time, initial concentrations were used to determine the adsorption capacity of modified clay. The effect of pH on adsorption was adjusted by using 0.1 mol/L HCl and 0.1 mol/L NaOH to vary the pH value from 2 to 12.

Additionally, the modified clay was regenerate by 0.053 mol/L $KAl(SO_4)_2 \cdot 12H_2O$ with the mass-volume of clay and regenerated liquid at 1:7.5 for 12 h. The regenerated adsorbent was then dried at 90 °C for 2 h and adopted following evaluation for its reusability. All adsorption experiments were carried out at the temperature of 10 ± 1 °C.

Results and discussion

Characterization of modified clay

The structure morphology and chemical composition of raw clay and modified clay was seen in SEM micrographs and EDS spectrum in Figs. 2a, b and 3a, b. The SEM micrographs of raw clay showed a dark colored and dense block structure (Fig. 2a). It can be seen from EDS spectrum that the elements of silicium, aluminum, calcium, oxygen, etc. were existed in raw clay (Fig. 2b). However, SEM micrographs of modified clay revealed that the dense structure of raw clay varied to loosen considerably (Fig. 3a). Moreover, the element peak of Lanthanum was appeared at the EDS spectrum of modified clay (Fig. 3b). The BET analysis also proved that the specific surface area of raw clay increased from 26.87 to 44.29 m²/g. The above data indicated that surface area was increased appreciably by modification.

The chemical elements of the raw clay, modified clay and the modified clay after fluoride ion adsorption were quantitatively estimated by XPS in Fig. 4a–c. The spectra of the raw clay exhibited two major element peaks at 536.1 and 74.6 eV, corresponding to O1 s and Al2p photoemission, respectively (Fig. 4a). Moreover, La³⁺ and Al³⁺ loaded modification made a new La3d peak at 851.2 eV, and that also caused the element peaks of O1s and Al2p moving to a lower and a higher energy side at 532.2 and 77.7 eV (Fig. 4b). After the fluoride adsorption onto modified clay, a new element peak which belongs to F1s at 677 eV was presented in Fig. 4c. Furthermore, the element peaks of O1s and Al2p continued to move toward a lower and a higher energy side of 0.4 and 0.1 eV compared with that of modified clay. This may be caused by interaction between fluoride ion and the modified clay which composed with lanthanum, aluminum and oxygen.

Kinetics and isotherms studies

To determine the equilibration time and to investigate the kinetic model for adsorption, the effect of connecting time on fluoride ion adsorption was investigated in this study. Figure 5 showed the relation between connecting time and amount of fluoride adsorbed on modified clay. It was observed that the adsorption rate of fluoride ion increased with time and kept steady after 600 min. Thus, the adsorption equilibrium time of adsorption was suggested as 600 min.

The common equations: pseudo-first order kinetic model and pseudo-second order kinetic model were used to fit the data of the kinetics of fluoride ion adsorption experiments (Biswas et al. 2009).

The pseudo-first order kinetic model of linear form equation is given by the following equation:

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1 t}{2.303} \tag{2}$$

The pseudo-second order kinetic model of linear form equation is given by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where k_1 is the pseudo-first-order rate constant of adsorption (1/min); k_2 is the pseudo-second-order rate constant of adsorption [g/(mg min)]; q_e and q_t are the amounts of fluoride adsorbed at equilibrium (mg/g) and at time t (min), respectively. The parameters were calculated and were shown in Table 1.

The rate constants value of pseudo-second order kinetic model (k_1) and pseudo-first-order kinetic model (k_2) usually represent the adsorption rate, which were 0.0117 and 0.1130, respectively. Larger k_2 value means lower adsorption rate of fluoride ion adsorption process onto

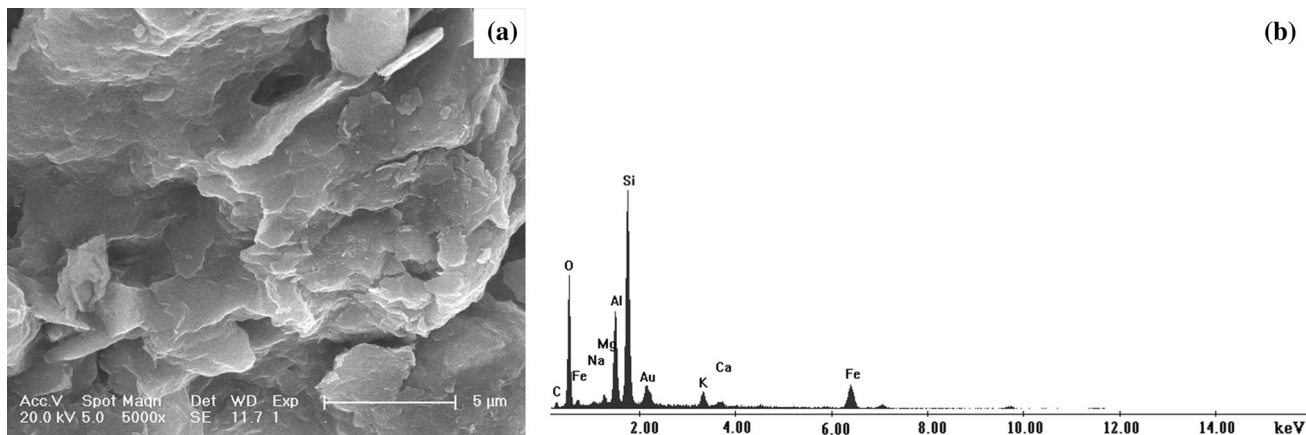


Fig. 2 SEM of raw clay (a) and EDS of raw clay (b)

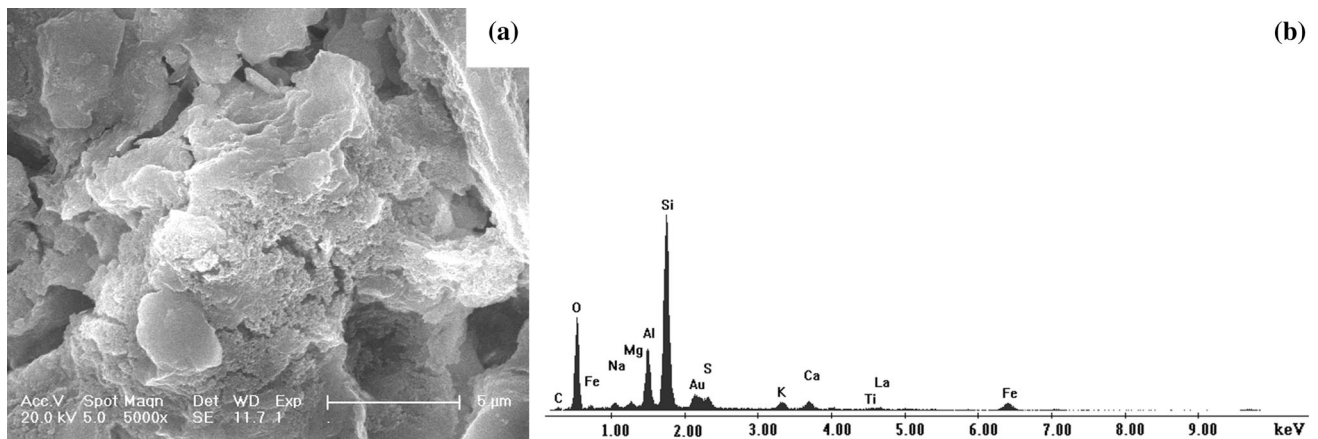


Fig. 3 SEM of modified clay (a) and EDS of modified clay (b)

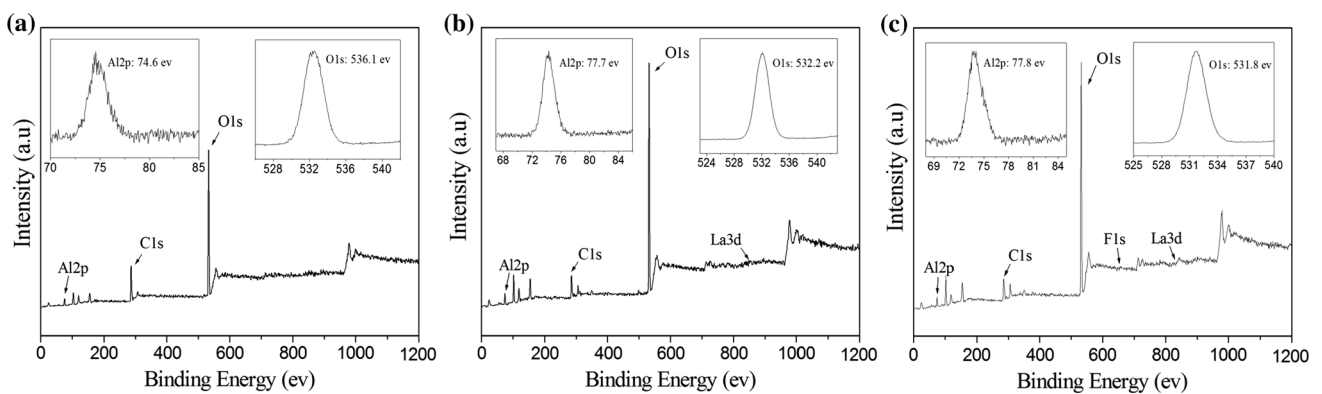


Fig. 4 XPS of raw clay (a), modified clay (b) and modified clay after adsorption of fluoride ion (c)

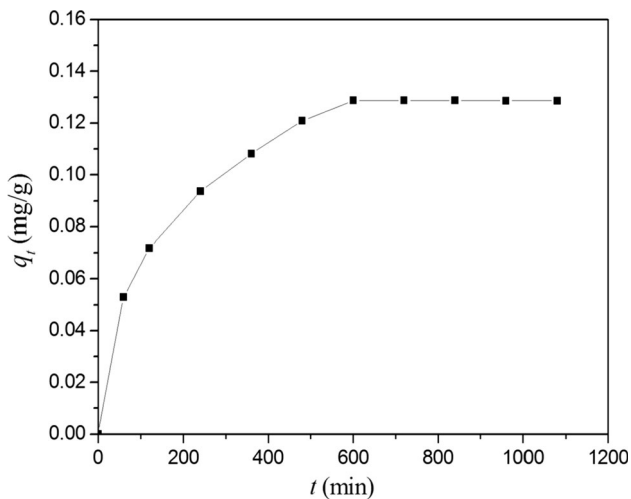


Fig. 5 Time vs. adsorption capacity with initial fluoride concentration of 4.89 mg/L

modified clay. The correlation coefficient values (R^2) of pseudo-first order and pseudo-second order kinetic model were 0.9819 and 0.9846, respectively. The calculated

Table 1 Kinetic parameters of fluoride ion adsorption onto modified clay

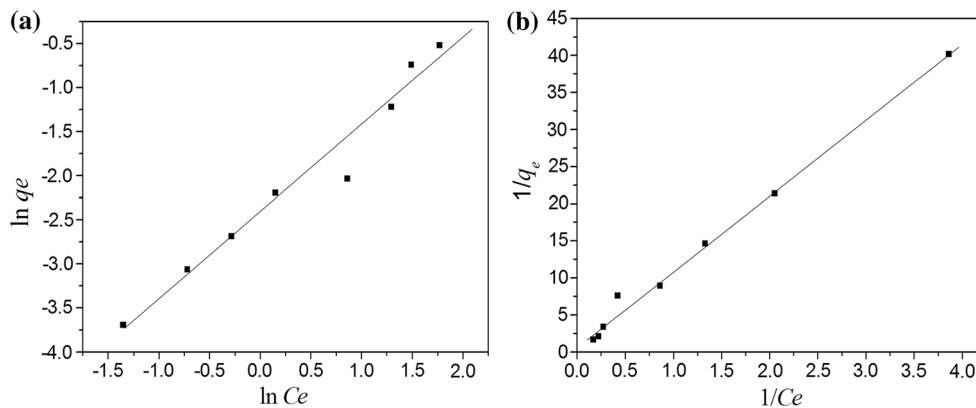
Pseudo-first order		Pseudo-second order	
Parameter	Value	Parameter	Value
k_1 (1/min)	0.0117	k_2 [g/(mg min)]	0.1130
q_e (mg/g)	0.1326	q_e (mg/g)	0.1716
R^2	0.9819	R^2	0.9846

adsorption capacity of pseudo-second order kinetic model was 0.1716 mg/g. It suggested that the fluoride ion adsorption process should be well described in accordance with the pseudo-second order kinetic model.

The applicability of Freundlich and Langmuir isotherm equations were tested on fluoride adsorption on modified clay (Gong et al. 2012). The Freundlich isotherm equation is given by the following equation:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K \tag{4}$$

Fig. 6 Freundlich adsorption isotherm (a) and Langmuir adsorption isotherm for the removal of fluoride ion by modified clay (b)



where q_e is the amount of fluoride ion adsorbed per unit weight of modified clay at equilibrium (mg/g), K and n are the Freundlich constants; C_e is the equilibrium concentration of fluoride ion in solution (mg/L).

The Langmuir equation was applied in the form:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{5}$$

where q_e is the amount of fluoride ion adsorbed per unit weight of modified clay at equilibrium (mg/g), Q_0 is the maximum adsorption capacity (mg/g), b is the Langmuir constant, and C_e is the equilibrium concentration of fluoride ion in solution (mg/L).

The results of isotherm experiment data was presented in linear forms to determine which model most accurately described adsorption process by modified clay in Fig. 6a, b. The adsorption capacity of adsorbent can be obtained from Freundlich constants (K and n) and the Langmuir constants (Q_0 and b). The correlation coefficients showed the experimental data was fitted to the Langmuir isotherms model ($R^2 = 0.9927$) better than that of Freundlich model ($R^2 = 0.9755$). The Freundlich isotherm model indicated that the fluoride ion adsorption process takes place on the non-uniformity modified clay surfaces. The values of the empirical constant K and n were calculated from Freundlich isotherm model, which were 0.0896 mg/g and 1.1096, respectively. However, the better Langmuir isotherm model fitting indicated that the monolayer adsorption process for fluoride ion was also valid onto the non-uniformity modified clay surface. The maximum adsorption capacity (Q_0) and constant related to the binding energy of the sorption system (b) were obtained from Langmuir isotherm fitting, which were 1.3033 mg/g and 0.0752 l/g, respectively.

Effect of pH

The removal of fluoride ions from groundwater was highly dependent on the pH. The effect of pH on fluoride removal

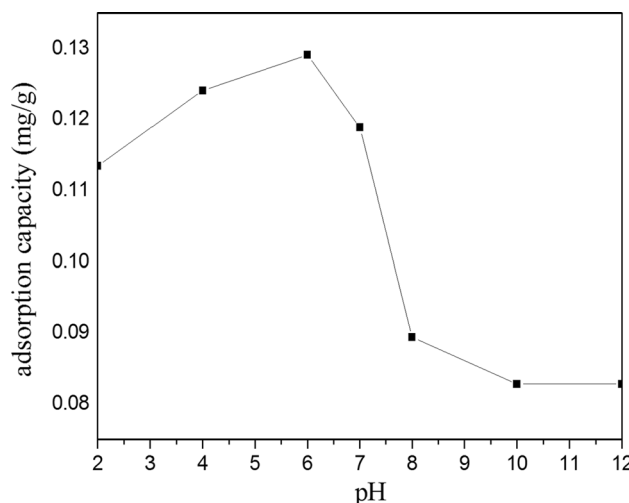


Fig. 7 Effect of pH on fluoride removal by modified clay

by modified clay was studied at various pH values from 2 to 12. Figure 7 showed the effect of pH on fluoride adsorption onto modified clay. The results indicated that the optimum pH value on fluoride ion adsorption was 6. This is mainly due to the pH would alter the surface charge of the modified clay, and the sensitive element of alumina favored fluoride in weak acidic environment. However, with the pH value increasing, the hydroxyl formed on the surface of modified clay intended to compete with fluoride ion for alumina exchange sites (Ghorai and Pant 2005), resulting in lower adsorption capacity.

Effect of regeneration

Chemically regeneration experiments were carried out to evaluate the reusability of the modified clay. The regeneration for modified clay was presented in Fig. 8. It can be seen from Fig. 8 that the regeneration rate of the modified clay descended with the regeneration cycle progressing. After six times' regeneration, the regeneration rate was still over 80 %, and the mass loss rate was also remained at a

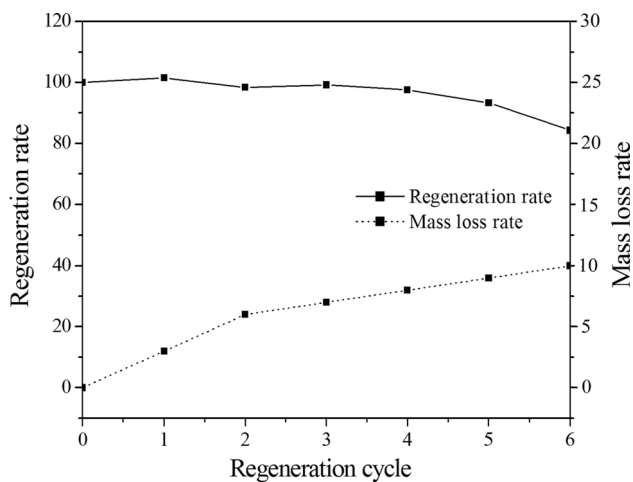


Fig. 8 The regeneration of modified clay

very low value (lower than 10 %). It showed that the modified clay could be well regenerated by $KAl(SO_4)_2 \cdot 12H_2O$ with the concentration of 0.053 mol/L.

Conclusion

Natural clay is an abundantly available mineral in many parts of the world. It can be synthesized to a new modified clay with high fluoride adsorption capacity. It was observed that the adsorption kinetics of modified clay could be described by pseudo-second order kinetic model. The adsorption isotherm experiment data were well fitted in Langmuir model and the maximum adsorption capacity of modified clay was 1.3033 mg/g. The optimum fluoride removal by modified clay was at pH of 6.0, and the modified clay could be well regenerated by $KAl(SO_4)_2 \cdot 12H_2O$. The performance of modified clay for fluoride ion removal in continuous flow fixed bed column experiment is in progress, which may provide the theoretic basis and data support for defluoridation with high fluoride concentration from groundwater in undeveloped regions.

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