Factors influencing the removal of fluoride from aqueous solution by calcined Mg–Al–CO$_3$ layered double hydroxides

Liang Lv [a,b], Jing He [a], Min Wei [a], D.G. Evans [a], Xue Duan [a,*]

[a] *Key Laboratory of Science and Technology of Controllable Chemical Reactions, Ministry of Education,*
Beijing University of Chemical Technology, Box 98, 15 Bei San Huan Dong Lu, Chao Yang District, Beijing 100029, China
[b] *The West Branch of Zhejiang University of Technology, Zhejiang 324006, China*

Abstract

Layered double hydroxides (LDH) calcined at different temperatures (denoted as CLDH) have been demonstrated to recover their original layered structure in the presence of appropriate anions. In the light of this so-called "memory effect", a study of removal of fluoride from aqueous solution by calcined Mg–Al–CO$_3$-LDH has been carried out. The LDH calcined at 500 °C had the highest capacity of removal of fluoride ion, because of retention of its intrinsic structure. The CLDH with an Mg/Al ratio of 2 has a remarkable ability to adsorb anions. The adsorption loading is higher for the calcined Mg–Al-LDH than for calcined Zn–Al and Ni–Al-LDH. The influence of varying the conditions for removal of fluoride, such as the pH of aqueous solution, the initial fluoride concentration, the dosage of adsorbent, and temperature on removal of fluoride have been investigated. The influence of co-existing anions in fluoride aqueous solution indicates that the percentage of removal of fluoride increased in order PO$_4$$^{3-}$ < Cl$^-$ ≈ SO$_4$$^{2-}$ < Br$^-$ ≪ NO$_3$$^-$. It was found that maximum removal of fluoride from aqueous solutions was obtained in 6 h at pH 6.0 with an initial concentration of 50 mg/L, and that the retention of fluoride ions by the CLDH material was 98% or higher. The residual fluoride concentration was found to be 0.4 mg/L with an initial concentration of 20 mg/L, which meets the national standard for drinking water quality. The Freundlich isotherm and Langmuir isotherm were used to fit the data of equilibrium experiments. The results of X-ray diffraction, FT-IR and TG-MS demonstrate that the adsorption phenomenon is accompanied by rehydration with concomitant uptake of fluoride ions to rebuild the initial layered structure.

1. Introduction

Fluorine in combined fluoride forms is naturally present in varying amounts in the atmosphere, water and soils. Fluoride ions can be found in wastewaters derived from glass industry, chemical industry, metal industry and high-tech industries such as manufacturing of semiconductors and integrated circuits [1]. The discharge of such wastewater into the surface water will lead to the contamination of groundwater. Long-term drinking of water containing high fluoride content can result in mottling of teeth, as well as softening of bones and ligaments. Many people in the world are affected by fluorosis, especially in China, India, Pakistan, and Thailand [2].

According to the World Health Organization guidelines [3], the maximum concentration limitation of fluoride is 1.5 mg/L for drinking water. However, the concentration found in groundwater is often higher than the standards. For example, concentration as high as 5 mg/L in Changzhou, China, have been reported [4]. Several methods have been tried to remove fluorides from water, namely adsorption [5–7], precipitation [2,8], electrodialysis [9], ion exchange [10] and electrochemical methods [11,12]. Of these, adsorption is still one of the most extensively used methods for defluoridation of water.

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds (HTlc) or anionic clays, consist of brucite-like hydroxide sheets, where partial substitution of trivalent for divalent cations results in a positive sheet charge compensated by anions within interlayer galleries [13]. Calcined Mg–Al–CO$_3$-LDHs have been demonstrated to reconstruct their original layered structure after adsorption of various

* Corresponding author. Tel.: +86 10 64425395; fax: +86 10 64425385.
E-mail address: duanx@mail.buct.edu.cn (X. Duan).

anions and are good ion exchangers/adsorbents for removal of toxic anions from contaminated water [14–21]. In the light of this so-called "memory effect" [22], removal of fluoride from aqueous solution by calcined LDHs was studied in this work.

Calcined LDHs (CLDH) were used as an adsorbent material. The effect of various factors such as (a) CLDH structure; (b) conditions for removal of fluoride, such as pH of aqueous solution, the dosage of adsorbent, initial concentration of fluoride, and temperature and (c) co-existing anions in fluoride aqueous solution on the removal of fluoride, have been investigated. The explanations of adsorption phenomena have been supported by X-ray diffraction, FT-IR and TG-MS results. It has also been shown that the LDH maybe regenerated after fluoride adsorption using Na_2CO_3 aqueous solution (0.1 mol/L).

2. Experimental

2.1. Materials

$Mg(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, Al $(NO_3) \cdot 9H_2O$, $NaNO_3$, NaOH, NaF, trisodium citrate dihydrate $(Na_3C_6H_5O_7 \cdot 2H_2O)$, glutin and urea were analytically pure reagents. All reagents were used without purification, and deionized water was decarbonated before use.

2.2. Preparation of LDH precursors and CLDH

$Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ with Mg^{2+}/Al^{3+} ratios of 2.0, 3.0 and 4.0 were dissolved in deionized water (25 mL) to obtain solutions (a); urea ([urea]/([Mg^{2+}]+ [Al^{3+}]) = 4.59) was dissolved in 25 mL water to obtain solution (b); glutin (3 g) was dissolved in 25 mL water to obtain solution (c). Then, solutions (a), (b) and (c) were mixed in a 100 mL autoclave with stirring for 20 min. The mixture was held at 130 °C for 6 h. The precipitate was washed throughly at 80 °C, and dried at 80 °C for 24 h to obtain the LDH. Finally, calcined Mg–Al-LDH (CLDH) was obtained by calcining LDH in a muffle furnace at the designated temperature for 2 h. Chemical composition indicates that the synthesized $Mg–Al–CO_3$ LDHs has Mg/Al molar ratios of 1.64:1, 2.65:1 and 3.51:1, less than the input ratio of 2.0:1, 3.0:1 and 4.0:1. It is known that LDHs synthesized by the urea method tend to be aluminium-rich [23,24]. Mg/Al molar ratios in the CLDH are 1.68:1, 2.66:1 and 3.47:1, indicating that calcination has no impact on the chemical composition as expected.

$Zn–Al–CO_3$-LDH and $Ni–Al–CO_3$-LDH were synthesized by a modified co-precipitation method as described elsewhere [25]. The method involves very rapid mixing to complete the nucleation process, followed by a separate aging process. $Zn(NO_3)_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ (0.36 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.18 mol) were dissolved in deionized water. A second solution containing NaOH (0.86 mol) and Na_2CO_3 (0.36 mol) in deionized water was prepared. The two solutions were simultaneously added to a colloid mill with a rotor speed of 5000 rpm. The resulting slurry was removed from the colloid

mill after 2 min and aged at 100 °C for a specified period. The final precipitate was filtered, washed thoroughly, and dried at 80 °C for 24 h.

2.3. Characterization

The CLDH materials before and after the adsorption of fluoride ions were characterized by X-ray diffraction, FT-IR and TG-MS. X-ray diffraction patterns of the samples were obtained using a Shimadzu XRD-6000 diffractometer with Cu Kα radiation (40 kV and 30 mA) at a scanning rate of 5°/min. FT-IR spectra of KBr pellets in the range 4000–400 cm^{-1} were recorded with a Bruker Vector 22 spectrometer. Elemental analysis was performed with a Shimadzu ICPS-7500 ICP instrument on solutions prepared by dissolving the samples in dilute HNO_3. TG-MS measurements were carried out on a Pyris Diamond TG/DTA instrument equipped with a mass spectrometer (ThermoStar TM) in an inert atmosphere. The temperature-programmed rate was 10 °C/min, and the measured range from 30 to 600 °C. Gaseous emission (HF, F_2, and CO_2) was analyzed at intervals of 1 s. Low-temperature N_2 adsorption-desorption experiments were carried out using a Quantachrome Autosorb-1 system. The surface area of the LDH precursor and CLDH were calculated using the BET method.

2.4. Determination of fluoride ion concentration

The concentration of fluoride ions in the solutions was determined using a selective electrode for fluoride ions [21], which measures concentrations from 10^{-6} M to saturated solutions. TISAB II (Total Ionic Strength Adjustment Buffer) was added to the solutions to reduce the variation in the ionic strength in the samples. This buffer contains a chelate, which forms complexes with other ions, such as iron and aluminum that could interfere in the determinations.

A calibration curve was obtained using NaF standard solutions with different fluoride concentrations from 1 to 10 mg/L. The results were plotted as fluoride concentration (mg/L) versus potential (mV).

2.5. Removal of fluoride ions

CLDH samples (2.0 g) were dispersed in 1.8 L of fluoride solutions containing 100 mg F$^-$/L and stirred for 5–6 h, with control of solution pH in an N_2 atmosphere. For the case of fluoride ion solutions, the experiments were carried out at initial pH 5.0, 6.0, 7.0, 8.0 and 10.0, which was adjusted using dilute nitric acid (1%) and was kept constant over the whole adsorption period. 2 mL samples were extracted, at selected time intervals, up to a maximum of 5–6 h, separated by filtration, and diluted to 50 mL. Fluoride ions were measured in the solution, and the solids remaining at the end of the experiment were characterized by X-ray diffraction, FT-IR and TG-MS. The fluoride concentration, the percentage removal of fluoride and the adsorption loading of CLDH were calculated. Equilibrium studies were conducted in a 500 mL flask by mixing 300 mL of fluoride solu-

Table 1
The effect of Mg/Al molar ratio and calcination temperature of LDH on removal of fluoride

Sample	Mg/Al ratio	Calcination temperature (°C)	Surface area (m²/g)	Pore diameter at maximum (nm)		Percentage removal (%)	Adsorption loading (mg/g)
1	2	200	76.8	2.35	6.80	69.88	65.46
2	2	400	122.2	2.66	7.20	77.86	69.51
3	2	500	240.6	3.72	10.5	85.53	80.12
4	2	600	213.6	2.45	20.3	66.55	62.34
5	2	800	39.9	2.27	33.4	53.24	49.87
6	3	500	223.3	2.41	9.54	73.43	64.60
7	4	500	208.5	2.15	7.68	72.29	63.60

tion with 0.333 g CLDH. The mixture was stirred at 30 °C for 24 h in an N_2 atmosphere.

3. Results and discussion

3.1. Effect of varying structure of CLDH

3.1.1. Calcination temperature of Mg/Al LDH

The adsorption of fluoride by LDH calcined at various temperatures was investigated. The adsorption was carried out by dispersing 2.0 g CLDH in a constant volume of 1.8 L fluoride aqueous solution, with initial concentration of fluoride 100 mg/L, under the condition of pH 6.0 and 30 ± 1 °C. The percentage of removal and adsorption loading of fluoride by LDHs calcined at different temperaturs are listed in Table 1. It can be seen from Table 1 that the adsorption loading of fluoride of LDH calcined at 500 °C is the highest, reaching 80 mg/g. It increases with calcination temperature between 200 and 500 °C, but decreases from 500 to 800 °C. Because LDH transforms to aluminum and magnesium oxides by lose of interlayer anions, the maximum adsorption loading of fluoride increases in the temperature range 200–500 °C. The interlayer carbonate of LDH is decomposed completely when calcined at 500 °C (see Fig. 1).
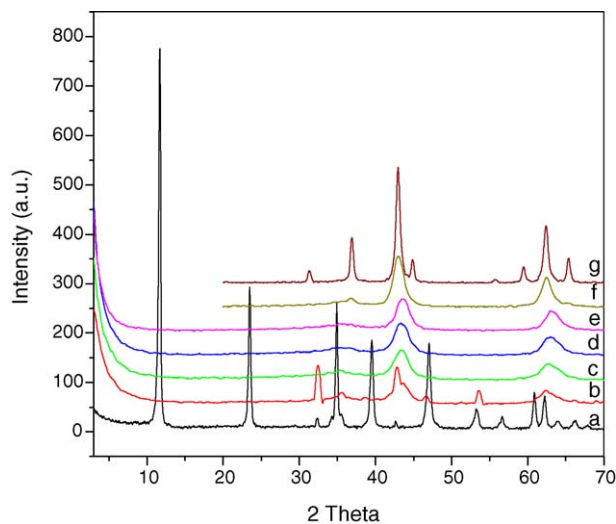
When the calcination temperature is above 500 °C, CLDH is transformed into a spinel that does not exhibit the property of reconstruction, which results in the observed decrease in the adsorption loading for anions.

3.1.2. Chemical composition of LDH layers

The effect of varying Mg/Al molar ratio on the removal of fluoride was also investigated. Table 1 and Fig. 2 show that the retention of fluoride by the CLDH with Mg/Al molar ratio 2 is the best of all, for which the adsorption content reached 80 mg/g. The adsorption content of fluoride by the CLDH with Mg/Al ratios of 3 and 4, are lower than the CLDH with Mg/Al ratio of 2, due to the higher charge density in the layers of CLDH with an Mg/Al ratio of 2 than with 3 and 4. As shown in Table 1, the specific surface areas of CLDH calcined at 500 °C are decrease with increasing Mg/Al ratio. This suggests that the retention of fluoride is also related to the surface area of CLDH.

The influence of metal cations in the LDH layers has also been studied. Fig. 3 indicates that the retention of fluoride by the Mg–Al-CLDH is higher than that of Ni–Al-CLDH and Zn–Al-CLDH. This is partly due to the lower anion exchange capacity of Ni–Al-CLDH and Zn–Al-CLDH, because of the higher atomic weight of Ni and Zn compared to Mg.

Fig. 1. XRD patterns of (a) uncalcined Mg–Al–CO₃ LDH, and Mg–Al–CO₃ LDH calcined at (b) 200 °C, (c) 400 °C, (d) 500 °C, (e) 600 °C, (f) 800 °C, (g) 1000 °C.
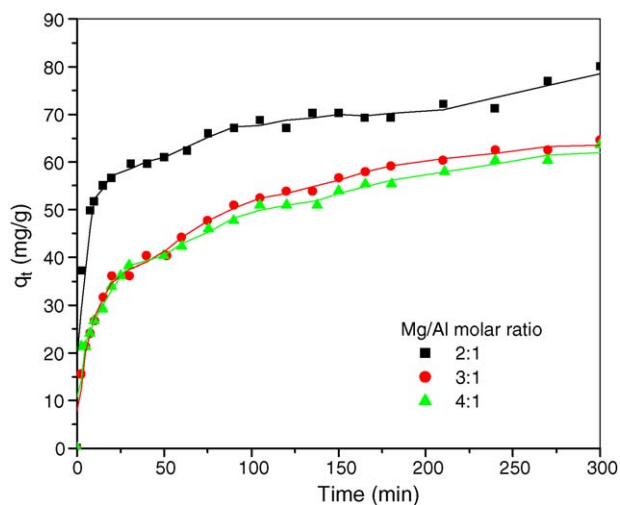

Fig. 2. Relationship between the adsorption loading of fluoride and the time, for CLDH with various Mg/Al molar ratios (V = 1.8 L, T = 30 °C, F⁻ = 100 mg/L, pH 6.0, $w_{adsorbent}$ = 2.0 g).
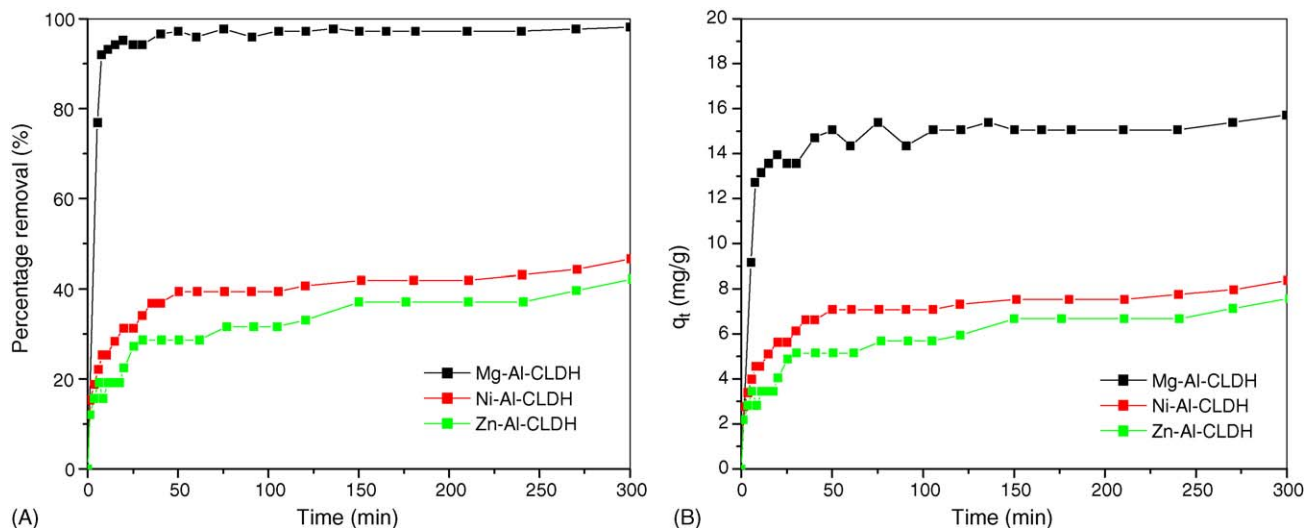
Fig. 3. Relationship between (A) the percentage removal of fluoride, (B) the adsorption loading of fluoride and the time, for CLDH containing various metal cations (V = 1.8 L, T = 30 °C, F⁻ = 20 mg/L, pH 6.0, $w_{adsorbent}$ = 2.0 g).

3.2. Effect of varying conditions for removal of fluoride

3.2.1. pH of aqueous solution

Generally, the pH is an important variable, which controls the adsorption at water-adsorbent interfaces. Therefore, the adsorption of fluoride on the CLDH was examined at different pH values ranging from 5.0 to 10.0 and relevant data are presented in Fig. 4. It can be seen from Fig. 4A that the percentage removal of fluoride is a maximum at pH 6.0, reaching 88.0%. Fig. 4B shows changes in the adsorption loading of fluoride with time for various pH values (5.0, 6.0, 7.0, 8.0, 10.0). It is obvious that fluoride ions are removed much faster at lower pH than at high pH. This result can be attributed to the increase in the concentration of competing anions OH⁻, at higher pH. The CLDH cannot

be used when the pH is lower than 5.0, however, because the layered material may be partly dissolved, leading to a decrease in adsorption loading.

3.2.2. The dosage of adsorbent

The effect of the dosage of adsorbent on the adsorption of fluoride with initial concentration of 100 mg/L was studied and the results shown in Fig. 5. It can be seen that the percentage removal increased with increasing dosage of adsorbent. The largest percentage removal was exhibited at 4.0 g CLDH per 1.8 L (90%) (see Fig. 5A). In Fig. 5B, it can be seen that the adsorption loading of fluoride decreases with increasing dosage of adsorbent. The adsorption loading of fluoride is the highest when the dosage of adsorbent is 2.0 (g/1.8 L). The
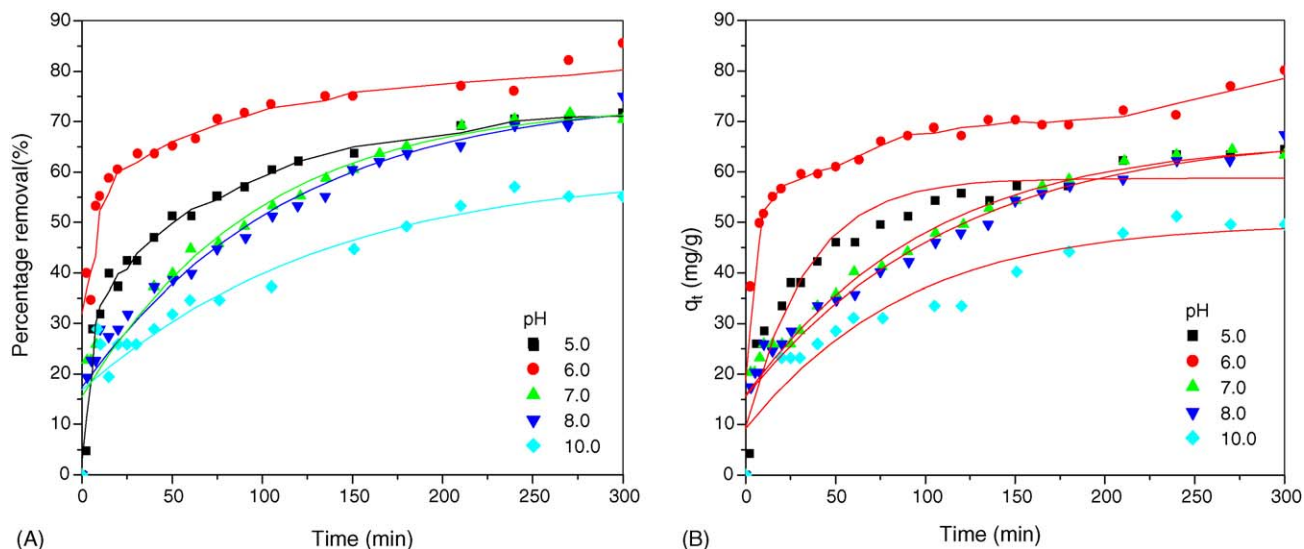

Fig. 4. Relationship between (A) the percentage removal of fluoride, (B) the adsorption loading of fluoride and the time, for various pH (V = 1.8 L, T = 30 °C, F⁻ = 100 mg/L, $w_{adsorbent}$ = 2.0 g).
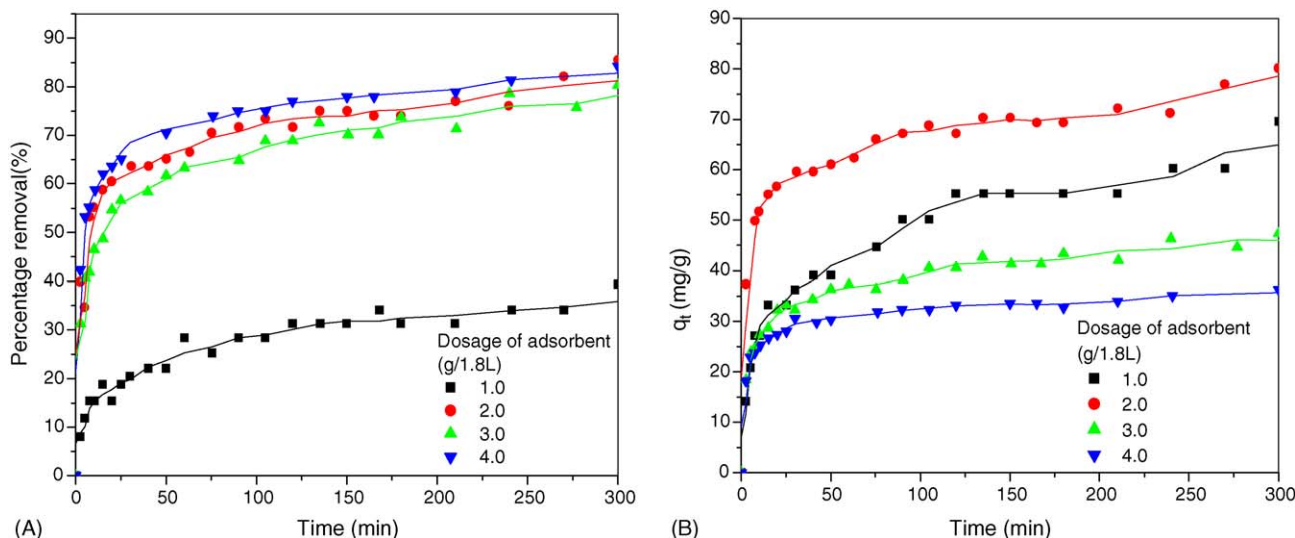
Fig. 5. Relationship between (A) the percentage removal of fluoride, (B) the adsorption loading of fluoride and time, for various dosages of adsorbent ($V = 1.8$ L, $T = 30\,^{\circ}$C, F$^-$ = 100 mg/L, pH 6.0).

influence of dosage of adsorbent is mainly related to its surface area.

3.2.3. The initial concentration of fluoride

The effect of varying the initial fluoride concentration on the process of adsorption for the CLDH (2.0 g) was studied and is shown in Fig. 6. It can be seen that the percentage removal of fluoride increases with decreasing initial fluoride concentration. The minimum residual concentration of fluoride obtained is 0.4 mg/L with an initial of 20 mgF$^-$/L, which reaches the standard for drinking water quality. Fig. 6B shows the relationship between the adsorption loading of fluoride and the time. When the initial concentration of fluoride is 200 mg/L, the adsorption loading of fluoride is the highest (138 mg/g); the residual concentration of fluoride however is 50 mg/L. Taking into account the percentage of removal, adsorption loading and residual amount of fluoride, it is possible to treat water to drinking standard quality (1.5 mg/L) by the use of CLDH when the initial concentration of fluoride is less than 20 mg/L.

The external mass transfer diffusion model and intraparticle diffusion model can be applied to investigate the effect of the boundary layer and intraparticle diffusion on the fluoride removal process. The external mass transfer diffusion model, as an application of Fick's laws, expresses the evolution of the concentration of the solute in the solution. The intraparticle mass transfer diffusion model has been extensively applied

in adsorbate–adsorbent systems. In this work the models chosen refer to theories developed by Weber and Morris [26] or McKay and Poots [27]. The initial rate of intraparticle diffusion is calculated by linearization of the curve $q_t = k_1 t^{0.5}$, where k_1 is the intraparticle diffusion constant [28].

Fig. 6C shows the variation of the adsorption loading and dimensionless concentration (C_t/C_0) versus time. For all the concentrations employed there is a monotonic increase in the adsorption loading with time. At low initial fluoride concentration, fluoride ion is almost removed completely from the aqueous solution. Thus, the overall adsorption process is not influenced by external mass transfer diffusion. The external mass transfer coefficients, β_L, can be obtained using the following equation [29]:

$$\ln\left(\frac{C_t}{C_0}\right) = -\left(\frac{\beta_L A}{V}\right) t \tag{1}$$

where A and V are the external surface area per unit mass and the bulk, respectively. The coefficients can be calculated from the data in the first 25 min when the solid surface fluoride concentration is much lower than the concentration in the solution. Increasing the initial fluoride concentration results in a decrease in the initial rate of external diffusion (Fig. 6C), but an increase in the intraparticle diffusion rate (Fig. 6D, Table 2). These results are consistent with the above results in that increasing the fluoride concentration in the solution seems to reduce the diffusion

Table 2
Effect of varying initial concentration on the diffusional constants in removal of fluoride by CLDH

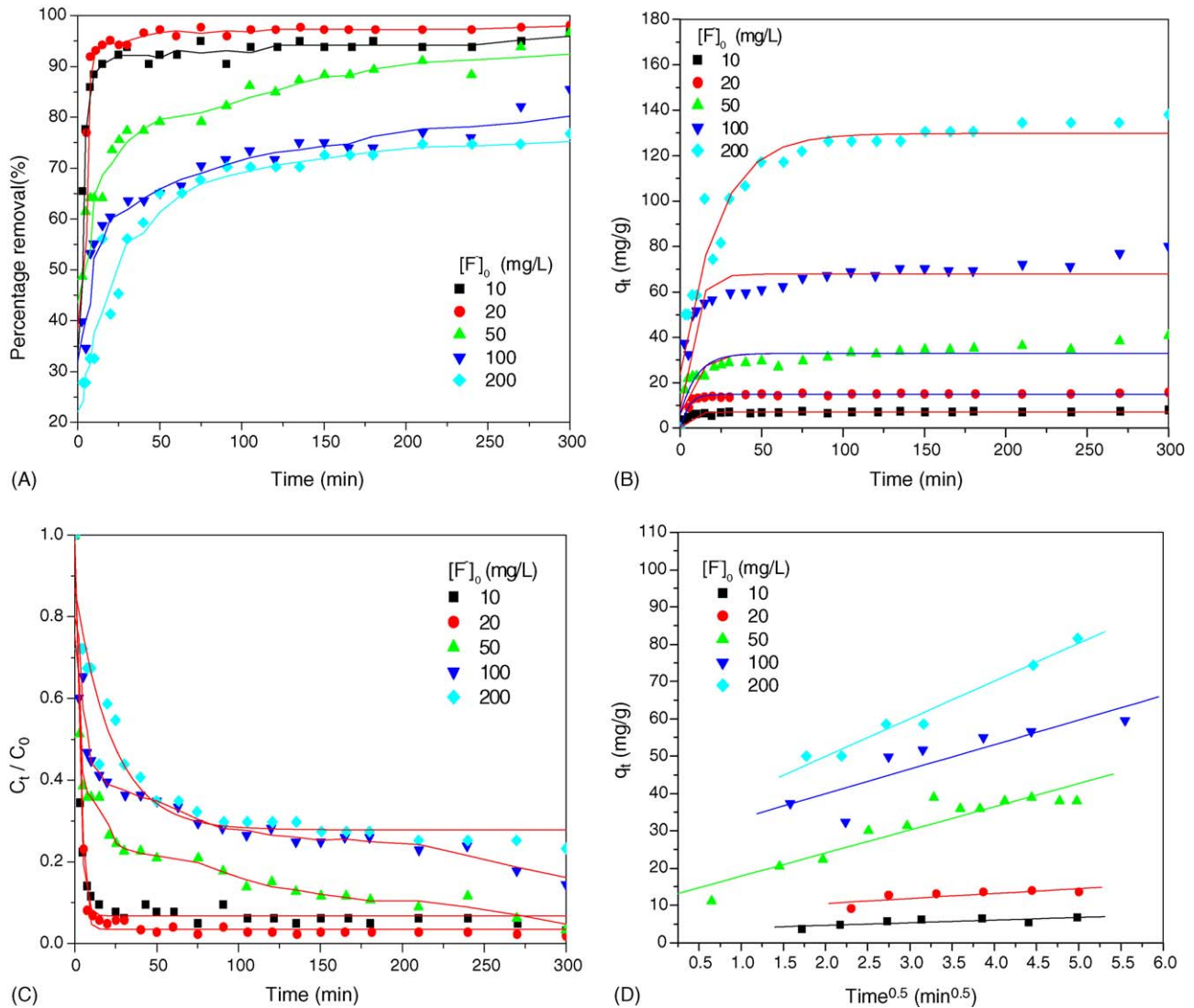| Initial F$^-$ concentration (mg L^{-1})	External diffusion		Intraparticle diffusion, W and M model k_1 (mg/g/min$^{0.5}$)
	$\beta_L A/V$ (min^{-1})	β_L ($\times 10^{-4}$ cm/min)	
10	0.0829	3.1010	0.7113
20	0.0886	3.3135	1.3297
50	0.0590	2.2077	6.2073
100	0.0498	1.8610	6.5824
200	0.0297	1.1099	10.0906

Fig. 6. Relationship between (A) the percentage removal of fluoride, (B) the adsorption loading of fluoride and the time, for various initial fluoride concentrations ($V = 1.8$ L, $T = 30$ °C, pH 6.0, $w_{adsorbent} = 2.0$ g), (C) external mass transfer resistance model, (D) intraparticle diffusion resistance model of Weber and Morris.

of fluoride ions in the boundary layer and to enhance the diffusion in the solid.

3.2.4. Temperature for removal of fluoride

Fig. 7 shows the adsorption curves obtained under different isothermal conditions. The apparent adsorption rate accelerates on raising the temperature. The rate of depletion of fluoride concentration at different temperatures shows that fluoride removal by CLDH follows second-order rate kinetics, satisfying an equation given by [30,31]:

$$\frac{t}{q_t} = \frac{1}{(k \times q_e^2)} + \frac{t}{q_e} \qquad (2)$$

where k (g/mg/min) is the rate constant for second-order kinetics, and q_e is the maximum adsorption loading. The values of the second-order rate constant k and q_e were calculated from the intercept and slope of the plots of t/q versus t. The linearity plots of t/q versus t indicate a good agreement of experimental q_e values with those derived from the second-order kinetic model.
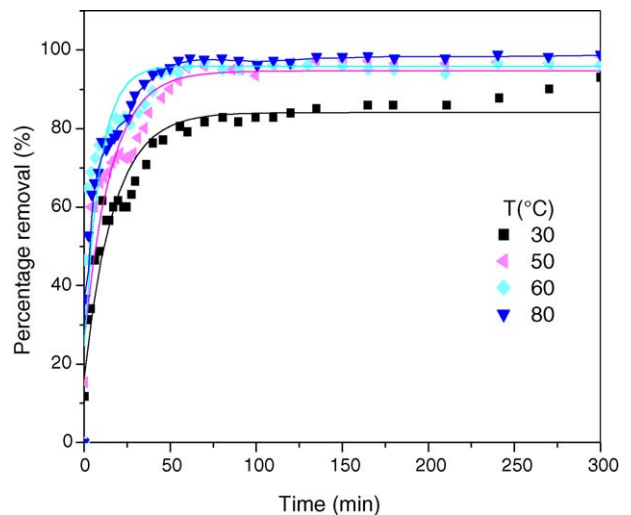

Fig. 7. Relationship between the percentage removal of fluoride and the time, for various temperatures ($V = 1.8$ L, pH 6.0, $F^- = 50$ mg/L, $w_{adsorbent} = 2.0$ g).
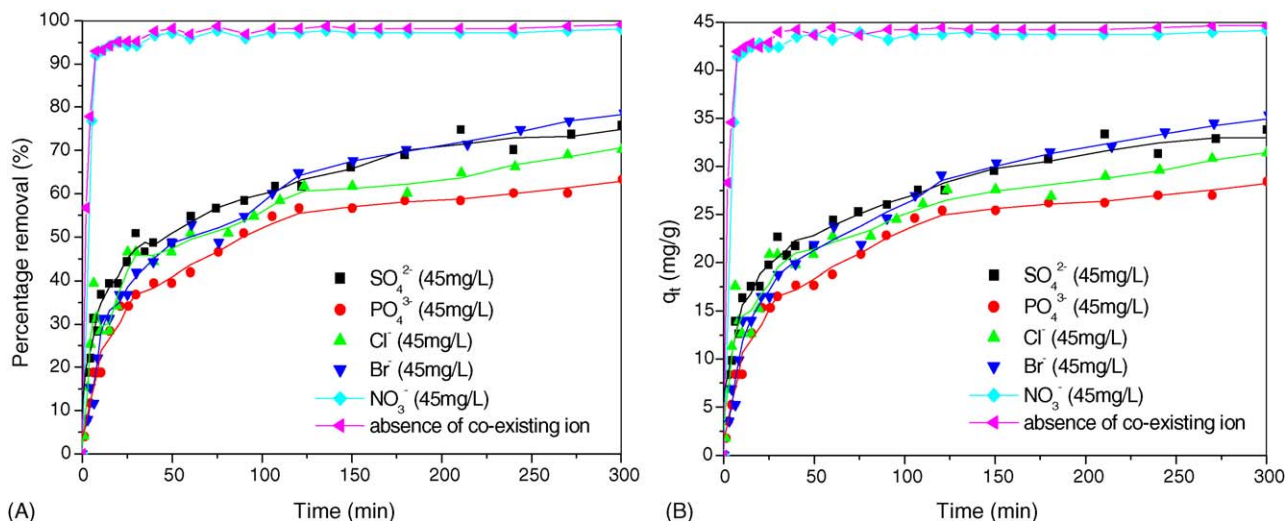
Fig. 8. Relationship between (A) the percentage removal of fluoride, (B) the adsorption loading of fluoride and the time, for various co-existing anions ($V = 1.8$ L, pH 6.0, $F^- = 50$ mg/L, $w_{adsorbent} = 2.0$ g).

The correlation coefficients for the second-order kinetic model are all larger than 0.99. The q_e values are calculated to be 46.02 49.41, 49.49, 50.35 mg/g at 30, 40, 50 and 60 °C, respectively, in agreement with the experimental data. The rate constants are calculated to be 4.846×10^{-3}, 7.727×10^{-3}, 1.044×10^{-2} and 2.134×10^{-2} g/mg/min at 30, 40, 50 and 60 °C, respectively. It can be seen that the rate of removal increases with the temperature of the aqueous solution.

3.3. Co-existing anions in fluoride aqueous solution

Drinking water contains many ions such as sulfate, phosphate, chloride, bromide and nitrate. They will compete with fluoride to be adsorbed onto CLDH. A constant volume of 1.8 L of 50 mg/L fluoride aqueous solution, containing 45 mg/L sulfate, phosphate, chloride, bromide or nitrate ions, was mixed with CLDH (2.0 g), at pH 6.0, and 30 ± 1 °C, for 5 h. It can be seen from Fig. 8 that nitrate hardly influences the fluoride removal, probably due to the fact that the interaction of NO_3^- with CLDH is weak. Fluoride removal in presence of other ions increased in the order $PO_4^{3-} < Cl^- \approx SO_4^{2-} < Br^- \ll NO_3^-$. The effect of these anions on fluoride adsorption may be due to their affinity towards CLDH which have greater affinities for anions with higher charge density. The Z/r (charge/radius) values of the anions varies in the order PO_4^{3-} (3/3.40) > SO_4^{2-} (2/2.40) > Cl^- (1/1.81) > Br^- (1/1.95) > NO_3^- (1/2.81), i.e., multivalent anions are adsorbed more readily than monovalent anions. On the other hand, the influence of chloride in this system is especially significant because the molar concentration of chloride ions is higher than those of other additive anions as a result of its low molar mass.

3.4. Equilibrium isotherms

Equilibrium studies were carried out to determine the optimum conditions for maximum fluoride removal by CLDH. Two general-purpose equilibrium models were used to fit the experimental data: (i) Langmuir (Eq. (3)) and (ii) Freundlich (Eq. (4)).

$$q_e = \frac{QbC_e}{(1 + bC_e)} \tag{3}$$

$$q_e = k_F C_e^n \tag{4}$$

where Q and b are the Langmuir constants related to the loading and energy of adsorption, k_F and n are the Freundlich temperature-dependent constants, C_e is the equilibrium concentration (mg/L), and q_e is the adsorption loading at equilibrium (mg/g), respectively.

Fig. 9 shows that the Freundlich isotherm is a better model than the Langmuir isotherm on the basis of the correlation coefficients ($R_F^2 = 0.9908$, $R_L^2 = 0.9714$). The best fit Freundlich parameters are $k_F = 15.16$, $n = 0.496$. The n value in the range of 0.1–1 indicates a favorable adsorption process. The best fit Langmuir parameters are $Q = 213.22$ mg/g, $b = 0.0479$ L/mg.
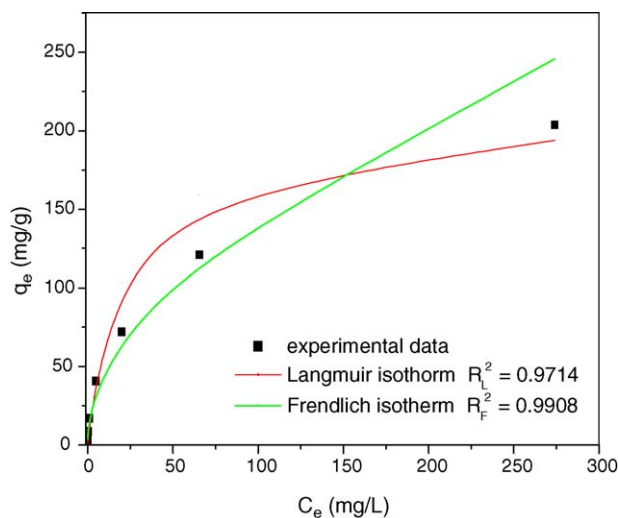

Fig. 9. Equilibrium isotherms for the removal of fluoride by CLDH at 30 °C. Experimental data are reported as points and models (Langmuir models and Freundlich models) by curves.
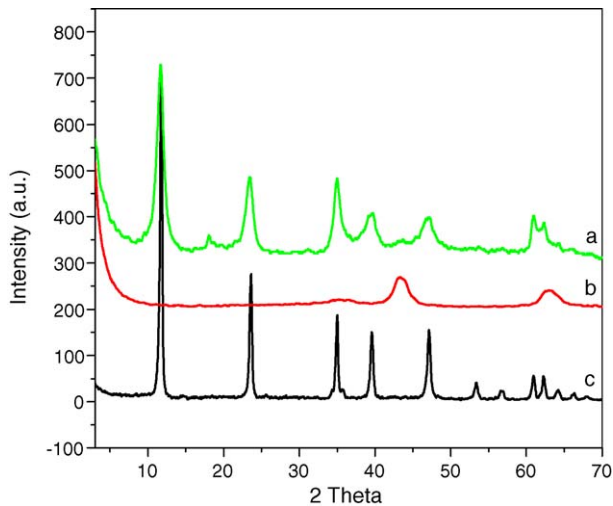
Fig. 10. XRD patterns of (a) CLDH after uptake of fluoride, (b) Mg–Al–CO$_3$-LDH calcined at 500 °C (c) Mg–Al–CO$_3$-LDH.

Fig. 11. FT-IR spectra of (a) CLDH after uptake of fluoride, (b) LDH calcined at 500 °C, (c) Mg–Al–CO$_3$-LDH.

The removal of fluoride by different adsorbents has been studied in recent years and some of these reports provide Q values. Although these values were obtained under different ranges of conditions, they can be useful in criterion of the adsorbent capacity. The Q value obtained in this study is greater than those of reported for alum sludge (5.394 mg/g) [32], actived alumina (16.34 mg/g) [33], flyash (20 mg/g) [34], lignite (7.09 mg/g) and bituminous coal (7.44 mg/g) [35].

3.5. Mechanism of removal of fluoride ions

Fig. 10 shows XRD patterns of CLDH after adsorption of fluoride ion, Mg–Al–CO$_3$ LDH and CLDH. The XRD patterns of the LDH calcined at 500 °C corresponds to that of a mixed aluminum magnesium oxide and the original LDH structure is regenerated after adsorption of fluoride. The re-constructed LDH exhibits a d_{003} basal spacing of 7.69 nm, larger than that of the original Mg–Al–CO$_3$-LDH (7.55 nm). Chemical analysis
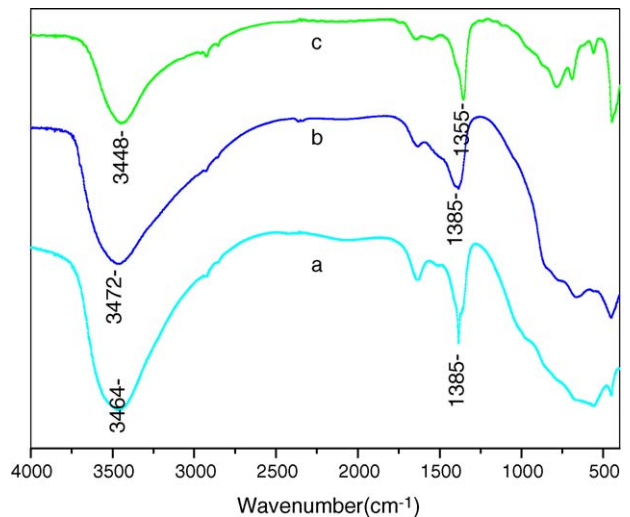
indicates that the CLDH after removal of fluoride has an Mg/Al molar ratio of 1.70:1, the same as that of the CLDH itself.

FT-IR spectra (see Fig. 11) show that a band is observed at 1355 cm^{-1} in the spectrum of Mg–Al–CO$_3$ LDH of the sample. This band is assigned to the vibrational absorption of interlayer CO$_3^{2-}$, as reported previously [12]. After calcination and adsorption of fluoride, this band shifts to higher frequency (see Fig. 11a) (1385 cm^{-1}). This could indicate surface adsorption of carbonate anions, which is a property of calcined LDHs [36]. The band betweens 400 and 800 cm^{-1} can be attributed to the superposition of the characteristic vibrations of magnesium and aluminum oxides. Three broad, very intense peaks at 3448, 3464, 3472 cm^{-1} could be due to hydrogen bonding.

The TG-MS measurements (see Fig. 12) show that the regenerated LDH has two stages of weight loss, corresponding to the decomposition of the interlayer anion—either fluoride or carbonate. The amount of HF (20) and F (19) from decomposition of fluoride in the LDH is higher than the amount of CO$_2$ (44)
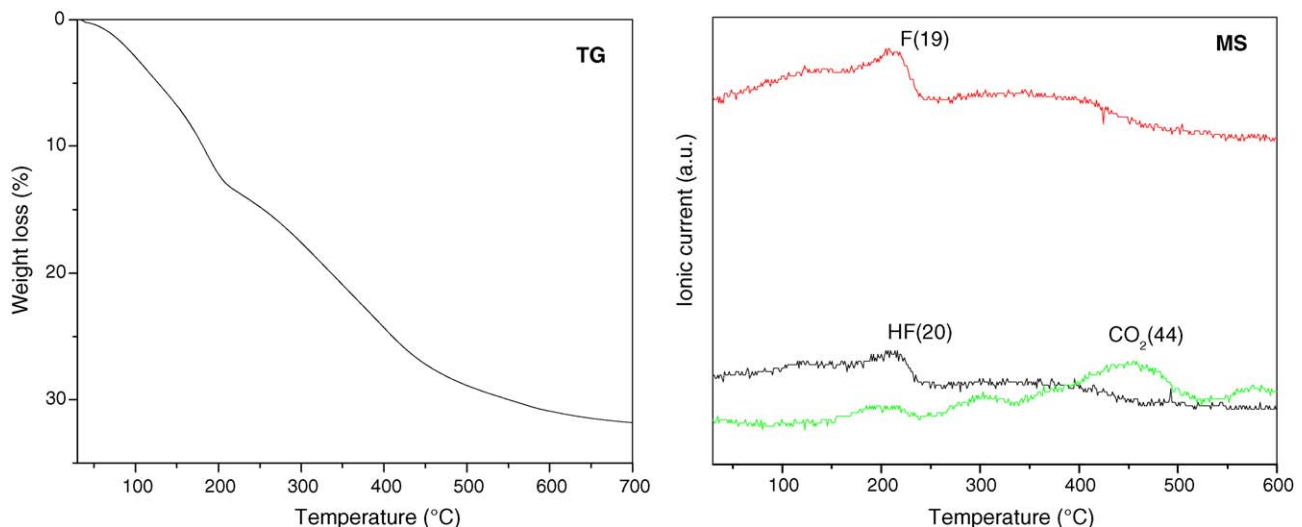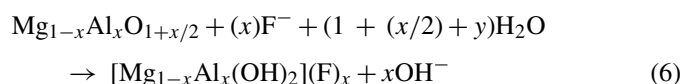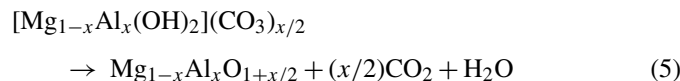

Fig. 12. TG-MS measurements of CLDH after uptake of fluoride.

arising from carbonate. It can be concluded that the interlayer anion in LDH after uptake of fluoride by CLDH is mainly fluoride.

The mechanism of removal of fluoride ions by calcined LDH can be explained as follows.

The regeneration of LDH is due to the ability of calcined LDH to incorporate anions into its structure by means of the so-called "memory effect". LDH containing carbonates as the interlayer anion decomposes into magnesium and aluminum oxides when heated at 500 °C. The calcined product $Mg_{1-x}Al_xO_{1+x/2}$ can be rehydrated and incorporate anions, such as fluoride, to rebuild the initial layered structure.

$$[Mg_{1-x}Al_x(OH)_2](CO_3)_{x/2}$$
$$\rightarrow Mg_{1-x}Al_xO_{1+x/2} + (x/2)CO_2 + H_2O \tag{5}$$

$$Mg_{1-x}Al_xO_{1+x/2} + (x)F^- + (1 + (x/2) + y)H_2O$$
$$\rightarrow [Mg_{1-x}Al_x(OH)_2](F)_x + xOH^- \tag{6}$$

OH^- is produced during rehydration of CLDH. As a result, controlling the pH of solution is important in order to maintain a driving force for removal of fluoride ion by CLDH.

The CLDH after removal of fluoride can be regenerated using Na_2CO_3 aqueous solution (0.1 mol/L) followed by calcination at 500 °C. It can be concluded from the above observations that the adsorption of fluoride is a reversible process, thereby facilitating the recylability of the material for further use.

4. Conclusions

The efficiency of a calcined Mg–Al–CO₃-LDH, as adsorbent to remove fluoride from aqueous solution, has been studied. The CLDH with an Mg/Al ratio of 2 has a marked ability to adsorb anions. The adsorption loading is higher for Mg–Al-CLDH than that for Zn–Al-CLDH and Ni–Al-CLDH. It was found that fluoride ions are removed much faster at low pH than at high pH. The adsorption rates decrease at low adsorbent concentration and hence more time is needed to reach equilibrium. The rate of removal increases with the temperature of aqueous solution. The influence of co-existing anions in fluoride aqueous solution indicates that the percentage of removal of fluoride increases in the order $PO_4{}^{3-} < Cl^- \approx SO_4{}^{2-} < Br^- \ll NO_3{}^-$. It was found that maximum removal of fluoride from aqueous solutions occurs at pH 6.0 in 5 h with an initial concentration of 50 mg/L, and that the retention of fluoride ions by the CLDH material was 98% or higher. The residual fluoride was found to be 0.4 mg/L with an initial concentration of 20 mg/L, which meets the national standard for drinking water quality. The rate constant k was calculated from the slope of the linear plots of t/q versus t, which is a second-order model. Equilibrum results could be fitted by the Freundlich isotherm and Langmuir isotherm, and the former is a better model. The Freundlich constant (n) in the range of 0.1–1 indicates a favorable adsorption process. The maximum adsorption capacity is 213.2 mg/g, higher than that reported on other adsorbents for fluoride removal. A mechanism of the adsorption

phenomenon has been proposed on the basis of X-ray diffraction, FT-IR and TG-MS. The results indicate that CLDH is a favorable absorbent for removal of fluoride.

Acknowledgements

References

[1] M. Mahramanlioglu, I. Kizilcikli, I.O. Bicer, Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth, J. Fluorine Chem. 115 (2002) 41–47.
[2] E.I. Reardon, Y.X. Wang, A limestone reactor for fluoride removal from wastewater, Environ. Sci. Tech. 34 (2000) 3247–3253.
[3] WHO (World Health Organization), Guidelines for drinking water quality, World Health Organization, Geneva 1 (1993) 45–46.
[4] M. Liu, R.Y. Sun, J.H. Zhang, N.Y. Bi, L. Wei, P. Liu, C.F. Kei, Elimination of excess fluoride in potable water with coarcervation by electrolysis using aluminium anode, Fluoride 20 (1983) 54–63.
[5] Q. Zhang, H. Liang, Aluminium phosphate for the defluorination of potable water, Environ. Int. 18 (1992) 307–310.
[6] N. Azbar, A. Turkman, Defluorination in drinking waters, Water Sci. Tech. 42 (2000) 403–407.
[7] E. Oguz, Adsorption of fluoride on gas concrete materials, J. Hazard. Mater. B 117 (2005) 227–233.
[8] A. Toyoda, T. Taira, A new method for treating fluorine wastewater to reduce sludge and running costs, IEEE Trans. Semiconductor Manuf. 13 (2000) 305–309.
[9] Z. Amor, B. Bernard, N. Mameri, M. Taky, S. Nicolas, A. Elmidaoui, Fluoride removal corn brackish water by electrodialysis, Desalination 133 (2001) 215–223.
[10] C. Castel, M. Schweizer, M.O. Simonnot, M. Sardin, Selective removal of fluoride ions by a two-way ion-exchange cyclic process, Chem. Eng. Sci. 55 (2000) 987–993.
[11] F. Shen, X. Chen, P. Gao, G. Chen, Electrochemical removal of fluoride ions from industrial wastewater, Chem. Eng. Sci. 58 (2003) 3341–3352.
[12] N. Mameri, A.R. Yeddou, H. Lounici, D. Belhocine, H. Grib, B. Bariou, Defluorination of septentrional Sahara water of north Africa by electrocoagulation process using bipolar aluminium electrodes, Water Res. 32 (1998) 1604–1612.
[13] F. Cavani, F. Trifiro, A. Vaccari, Hydrotalcite-type anionic clays: preparation, properties and applications, Catal. Today 11 (1991) 173–301.
[14] J. Orthman, H.Y. Hu, G.Q. Lu, Use of anion clay hydrotalcite to remove coloured organics from aqueous solution, Sep. Purif. Tech. 31 (2003) 53–59.
[15] R.L. Goswamee, P. Sengupta, K.G. Bhattacharyya, D.K. Dutta, Adsorption of Cr(VI) in layered double hydroxides, Appl. Clay Sci. 13 (1998) 21–34.
[16] N.K. Lazaridis, D.D. Asouhidou, Kinetics of sorptive removal of chromium (VI) from aqueous solutions by calcined Mg–Al–CO₃ hydrotalcite, Water Res. 37 (2003) 2875–2882.
[17] M.C. Hermosin, I. Pavlovic, M.A. Ulibabrri, J. Cornejo, Hydrotalcite as sorbent for trinitrophenol: sorption capacity and mechanism, Water Res. 30 (1996) 171–177.
[18] T. Toraishi, S. Nagasaki, S. Tanaka, Adsorption behavior of $IO_3{}^-$ by $CO_3{}^{2-}$ and $NO_3{}^-$ hydrotalcite, Appl. Clay Sci. 22 (2002) 17–23.
[19] M.A. Ulibarri, I. Pavlovic, M.C. Hermosin, J. Cornejo, Hydrotalcite-like compounds as potential sorbents of phenols from water, Appl. Clay Sci. 10 (1995) 131–145.
[20] D.P. Das, J. Das, K. Parida, Physicochemical characterization and adsorption behavior of calcined Zn/Al hydrotalcite compound (HTlc) towards removal of fluoride from aqueous solution, J. Colloid Interface Sci. 261 (2003) 213–220.

[21] C. Diaz-Nava, M. Solache-Rios, M.T. Olguin, Sorption of fluoride ions from aqueous solutions and well drinking water by thermally treated hydrotalcite, Sep. Sci. Tech. 38 (2003) 131–147.

[22] Z.F. Ren, J. He, C. Zhang, X. Duan, Removal of chloride anion by calcined layered double hydroxides, Fine Chem. 19 (2002) 339–342.

[23] P.P. Yang, J.F. Yu, T.H. Wu, G.Z. Liu, T.S. Chang, D.K. Lee, D.H. Cho, Urea decomposition method to synthesize hydrotalcites, Chin. Chem. Lett. 15 (2004) 90–92.

[24] M. Adachi-Pagano, C. Forano, J.P. Besse, Synthesis of Al-rich hydrotalcite-like compounds by using the urea hydrolysis reaction—control of size and morphology, J. Mater. Chem. 13 (2003) 1988–1993.

[25] X. Duan, L. Li, Q.Z. Jiao, Chinese Patent CN9,911,385, 1999.

[26] W.J. Weber, J.C. Morris, Advances in water pollution research: Removal of biologically-resistant pollutants from waste waters by adsorption, in: Proc. Int. Conf. on Water Pollution Symp., vol. 2, 1962, pp. 231–266.

[27] G. McKay, V.J.P. Poots, Kinetics and diffusion process in colour removal from effluent using wood as an adsorbent, J. Chem. Tech. Biotech. 30 (1980) 279–292.

[28] M. Jansson-Charrier, E. Guibal, J. Roussy, Vanadium sorption by chitosan: kinetics and equilibrium, Water Res. 30 (1996) 465–475.

[29] J. Buffle, N. Parthasarathy, W. Haerdi, Importance of speciation methods in analytical control of water treatment processes with application to fluoride removal from waste waters, Water Res. 19 (1985) 7–23.

[30] Y.S. Ho, G. Mckay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.

[31] C. Namasivayam, S. Sumithra, Adsorptive removal of catechol on waste Fe(III)/Cr(III) hydroxide: equilibrium and kinetics study, Ind. Eng. Chem. Res. 43 (2004) 7581–7587.

[32] M.G. Sujana, R.S. Thakur, S.B. Rao, Removal of fluoride from aqueous solution by using alum sludge, J. Colloid Interface Sci. 206 (1998) 94–101.

[33] A. Howard, K. George, F.K. Lindsay, Removal of fluorides from potable water by tricalcium phosphate, Ind. Eng. Chem. 30 (1938) 163–165.

[34] A.K. Chaturvedi, K.P. Yadav, K.C. Pathak, V.N. Singh, Defluoridation of water by adsorption on flyash, Water Air Soil Pollution 49 (1990) 51–61.

[35] A. Sivasamy, K.P. Singh, D. Mohan, M. Maruthamuthu, Studies on defluoridation of water by coal-based sorbents, J. Chem. Tech. Biotech. 76 (2001) 717–722.

[36] J.I.D. Cosimo, V.K. Díez, M. Xu, E. Iglesia, C.R. Apesteguía, Structure and surface and catalytic properties of Mg–Al basic oxides, J. Catal. 178 (1998) 499–510.