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Fluoride removal by Ca-Al-CO_3 layered double hydroxides at environmentally-relevant concentrations

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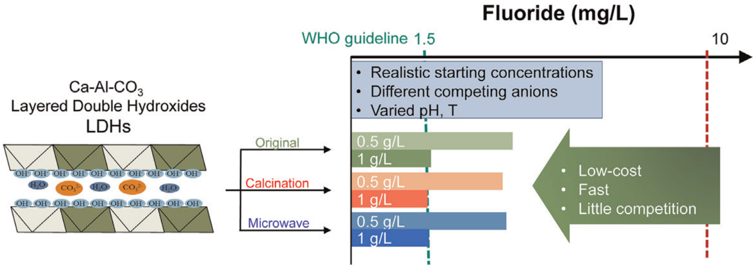
HIGHLIGHTS

- Ca—Al—CO_3 layered double hydroxides showed affinity for F^- at 2—12 mg/L.
- A higher F^- removal capacity at lower pH and lower temperature was observed.
- Only marginal defluorination improvements by calcination/microwave treatment.
- Fast F^- uptake during the initial 20 min and little anions competition was observed.
- F^- removal capacity is not necessarily reflected in specific surface area.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, F^- removal by Ca—Al—CO_3 layered double hydroxides (LDHs) was investigated at environmentally-relevant concentration ranges (2—12 mg/L) to below the WHO guideline, with an emphasis on the effect of LDHs' modification, as well as the effects of initial F^- concentration, adsorbent dose, pH, temperature and co-existing ions. Ca—Al—CO_3 LDHs, either untreated, calcined or microwave treated, showed affinity for the removal of F^- from synthetic groundwater with capacities of 6.7—8.4 mg F^-/g LDHs at groundwater-relevant pH, with a higher F^- removal capacity at lower pH (<8) and lower temperature (12 °C, as compared to 25 °C & 35 °C). Since calcination and microwave treatment resulted in only marginal defluorination improvements, using untreated LDHs appears the practically most feasible option. For the untreated LDHs, competition with Cl^- and NO_3^- was not observed, whereas at higher HCO_3^- and SO_4^{2-} concentrations (>250 mg/L) a slight reduction in F^- removal was observed. This study indicates the potential of Ca—Al—CO_3 LDHs as a cost-effective F^- removal technology, particularly when locally sourced and in combination with low-cost pH correction.

1. Introduction

Fluoride (F^-) is essential for the growth of teeth and bones, but excessive F^- intake causes dental and skeletal fluorosis (Edmunds and Smedley, 2013). Fluorosis caused by F^- contamination of groundwater has been reported in 35 nations over the world from Africa, South Asia, the Middle East, North, Central and South America, and Europe (Ayoob et al., 2008). Although a multitude of technologies such as coagulation, adsorption, ion exchange, electrochemical, and membrane processes have been investigated for

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F^- removal and some of them showed promising F^- removal capacities, many of them indulge in high installation and maintenance costs, complex treatment processes, and by-product pollutants (Ayoob et al., 2008; Osterwalder et al., 2014; Bhatnagar et al., 2011). Adsorption is a preferable F^- removal method because of the ease of operation, cost-effectiveness, and potential effective F^- removal capacity, especially for developing countries (Mohapatra et al., 2009; Kanno et al., 2014).

Layered double hydroxides (LDHs) are a class of anionic clays that are being applied in various fields such as flame-retardant fillers, catalysts, drug carriers and adsorbents (Li and Duan, 2006). LDHs have attracted considerable attention because of their potential high defluoridation capacity and cost-effectiveness (Sun et al., 2017). The general formula of LDHs is $[M^{2+}{}_{1\text{-}x}M^{3+}{}_{x}(OH)_2]^{x+}$ $[A^{m-}{}_{x/m} \cdot nH_2O]$, where M^{2+} corresponds to a divalent metal, such as Mg^{2+}, Zn^{2+} or Ni^{2+}, M^{3+} corresponds to a trivalent metal, such as Al^{3+}, Fe^{3+} or Cr^{3+}, x is the ratio of $M^{3+}/(M^{2+}+M^{3+})$, and A^{m-} corresponds to an exchangeable anion such as CO_3^{2-}, Cl^-, NO_3^- (Cavani et al., 1991; Ingram and Taylor, 1967). The presence of a large number of exchangeable anions and sizable interlayer spaces makes LDHs attractive for the removal of dissolved contaminants from water (Mandal and Mayadevi, 2008a), including F^-, Cl^-, NO_3^-, BrO_3^-, PO_4^{3-}, As(III), Pb(II), Cr(VI), Cu(II) and Cd(II) (Batistella et al., 2011; Chitrakar et al., 2011; Halajnia et al., 2012; Das et al., 2006; Lazaridis et al., 2004; Pérez et al., 2006; Caporale et al., 2013; Lv et al., 2009). In order to enhance the removal capacity of LDHs, several methods have been used to modify LDHs, such as metal oxide amendment, acid treatment and thermal activation (Batistella et al., 2011; Lv, 2007; Zhang et al., 2013). Thermal treatment using a muffle furnace (Lv, 2007), so-called calcination, causes the destruction of the layered structure of LDHs, however, this structure is afterwards recovered upon hydration (Ma et al., 2011). Microwave radiation heating is an alternative method that heats the material from inside out (Bhatnagar et al., 2013), and has been applied for activated carbons (Yuen and Hameed, 2009). Microwave radiation would reduce the treatment time compared to calcination, consequently resulting in reduced energy consumption and CO_2 emission (Huang et al., 2011). Microwave treatment has been applied for synthesis and construction research (Benito et al., 2009), but not for LDHs' modification.

Different types of LDHs have been studied for the removal of F^- from aqueous solutions, e.g., Mg–Al, Ni–Al, Zn–Al, Li–Al, Mg–Cr, Mg–Fe, Fe–Mg–Al LDHs (Batistella et al., 2011; Wang et al., 2007; Kameda et al., 2015; Chang et al., 2011; Lv et al., 2007; Du et al., 2014; Mandal and Mayadevi, 2008b). However, most of the previous studies were carried out at high initial F^- concentration (>50 mg/L), whereas F^- concentrations in actual groundwater ranges from 0.1 to 22 mg/L, and most frequently below 10 mg/L (Wen et al., 2013). In addition, F^- concentrations need to be reduced to <1.5 mg/L to comply with the World Health Organisation (WHO) guideline for drinking water (World Health Organization, 2004). Among the various types of LDHs, Mg–Al LDHs and their calcined products are the most studied. However, F^- removal by Ca–Al LDHs and their modified products is rarely reported, while Ca–Al LDHs is expected to have a better defluorination efficiency than Mg–Al LDHs considering the affinity of calcium and aluminum towards F^- (Ghosal and Gupta, 2015).

It was the aim of this study to investigate whether Ca–Al–CO_3 LDH is a suitable alternative for F^- removal from groundwater, specifically in the low, environmentally-relevant initial F^- concentration range (2–12 mg/L), to concentrations below the WHO guideline. For this reason, the performance of Ca–Al–CO_3 LDH as F^- adsorbent was investigated under different environmentally-relevant water compositions (including, initial F^- concentration, pH, temperature and co-existing ions). In addition, calcination and microwave treatment were investigated as Ca–Al–CO_3 LDH modification methods with respect to their effect on LDH surface properties (including, XRD, FTIR, BET and pH_{zpc}).

2. Materials and methods

2.1. Chemicals and materials

All reagents including HCl, NaOH, NaF, NaCl, $NaNO_3$, $NaHCO_3$ and Na_2SO_4 were of analytical grade (Sigma-Aldrich). Deionized water was used throughout the experiments and treatment processes. $Ca_4Al_2(OH)_{12}CO_3 \cdot nH_2O$ (n = 4–5) LDH (ACTILOX®CAHC) was obtained from Nabaltec (Germany) with a Ca/Al ratio of 1.86. Before use, Ca–Al–CO_3 LDHs was dried in an oven at 105 °C for 12 h.

2.2. Calcination and microwave treatment of LDHs

The calcined Ca–Al–CO_3 LDHs were obtained by calcining Ca–Al–CO_3 LDHs (5 g) in a muffle furnace at 500 °C for 2 h and cooling in a desiccator. Microwave radiation heating was carried out in a commercial microwave oven with 1000 W output at 2450 MHz (Samsung MS28J5215AB) with suitable adjustment (Supplementary Information (SI), Fig. S1). The microwave treatment was carried out in a quartz bowl fixed in the chamber of the microwave oven. The temperature of the LDHs after microwave irradiation was measured immediately after treatment, using an infrared radiation thermometer (TROTEC BP21). 5 g of Ca–Al–CO_3 LDHs sample was treated by microwave irradiation for 15 min and then cooled in a desiccator to room temperature for further use.

2.3. Characterization methods

The crystalline structure of Ca–Al–CO_3 LDH and its modified products before and after the experiments was characterized using a Philips PW 1830 powder X-ray diffractometer with a 2θ range of 5–70°. Fourier transform infrared spectroscopy (FTIR) spectra of Ca–Al–CO_3 LDH and its modified products were recorded by a fourier transform infrared spectrometer (Spectrum TM 100 Optical ATR-FTIR), following pelletization of the materials. The textural properties of Ca–Al–CO_3 LDH and its modified products were characterized using a surface area analyzer (Micrometrics Gemini VII 2390 V1.03). Brunauer-Emmett-Teller (BET) surface areas of Ca–Al–CO_3 LDH and its modified products were determined by N_2 adsorption-desorption method. The pore-size distribution was determined by the Barret-Joyner-Halender (BJH) method.

The pH at the point of zero charge (pH_{zpc}) of Ca–Al–CO_3 LDH and its modified products was determined by the pH drift method (Müller et al., 1985). The initial pH of NaCl (0.01 mol/L) was adjusted from 3.0 to 13.0 by addition of 0.1 mol/L HCl or NaOH, followed by LDHs sample (0.1 g) addition to the solution. After stirring at room temperature for 24 h, the final pH (pH_{final}) was measured. The pH_{zpc} of the Ca–Al–CO_3 LDH and its modified products was determined from the plots pH_{final} versus $pH_{initial}$. The point at which pH_{final} equal $pH_{initial}$ was taken as the pH_{pzc}.

2.4. Batch adsorption experiments

A stock solution of F^- (NaF as 1000 mg F^-/L) was diluted to different working solutions. For adsorption isotherm experiments, Ca–Al–CO_3 LDH and its modified products (0.1 g) were dispersed in 100 mL of F^- solutions (2–12 mg F^-/L), with the pH being adjusted to 8 at the experiment start using HCl (1 M). After stirring (Magnetic stirrer at 100 rpm) for 24 h, the solutions were filtered by a microfiltration membrane (0.45 μm). The concentrations of F^- were analyzed by Metrohm 881 ion chromatography (IC) with a Metrosep A Supp 5 column (eluent: 3.2 mM Na_2CO_3 and 1 mM $NaHCO_3$; flow rate: 0.7 mL/min). The effects of batch adsorption parameters including pH, adsorbent dose, co-existing anions, were investigated at an initial F^- concentration of 10 mg/L. The effect of initial pH was investigated at 6, 7, 8, 9, and 10 (±0.1). The effect of adsorbent dose was studied at pH 8 with adsorbent doses of 0.1, 0.2, 0.5, 1, 1.5 and 2 g/L. The batch experiments of the effect of temperature were carried out at different temperatures (12 ± 1, 25 ± 1 and 35 ± 1 °C). The effect of co-existing anions (Cl^-, NO_3^-, HCO_3^-, SO_4^{2-}) on F^- adsorption was studied by varying their concentrations (0, 50, 100, 250, 500 mg/L) with an initial F^- concentration of 10 mg/L at pH of 8, by dosing NaCl, $NaNO_3$, $NaHCO_3$ and Na_2SO_4. For kinetic studies, Ca—Al—CO_3 LDHs samples (1 g) were dispersed in 1 L F^- solutions (10 mg/L) and stirred for 5 h under the initial pH of 8. Samples (3 mL) were collected at selected time intervals (0, 1, 2, 3, 4, 5, 10, 20, 30, 40, 50, 60, 120, 180, 240 and 300 min), then filtered and analyzed as mentioned before.

The F^- uptake (q: mg/g) at equilibrium and non-equilibrium contact times was calculated using the following equation:

$$q = \frac{(c_0 - c)V}{m} \tag{1}$$

where C_0 and C are initial and F^- concentrations after the experiment (mg/L), respectively; V (L) is the solution volume; and m (g) is the adsorbent mass.

An overview of experimental conditions is given in Table 1. All the batch experiments and kinetic studies were carried out in duplicates. For the results of isotherm, the averaged data were reported.

2.5. Adsorption isotherm and kinetic models

Assuming strictly adsorptive removal processes, the equilibrium data were fitted by the Langmuir and Freundlich isotherm models. The kinetic models can be used to investigate the possible mechanism of adsorption and potential rate controlling steps (Gupta and Bhattacharyya, 2011). Four most commonly used models, namely the pseudo-first-order, pseudo-second-order, the Elovich equation, and the intraparticle diffusion models were fitted to the kinetic experimental data. Details on the equations and plotting can be found in the SI.

The fitting of experimental data to adsorption isotherm and kinetic models was accomplished by using OriginPro 9.0. The calculation of saturation-index of calcium fluoride (CaF_2) was carried out on PHREEQC (Dhiman and Keshari, 2006; Parkhurst and Appelo, 2013). Detailed descriptions of simulation can be found in the SI.

3. Results and discussion

3.1. Characterization of Ca—Al—CO_3 LDHs

The differences in chemical and physical properties of untreated, calcined and microwave treated Ca—Al—CO_3 LDHs were compared by XRD, FTIR, and N_2 gas adsorption to study the effects of modification. Table 2 shows the BET surface area, pore volume, pore diameter and pH_{pzc} of Ca—Al—CO_3 LDH and its modified products. The surface area was less than 10 m^2/g, which is lower compared to other inorganic sorbents, such as activated alumina (250 m^2/g) (Ghorai and Pant, 2004). After calcination, the surface area decreased slightly while the average pore size increased. Both calcination and microwave treatment increased the pore volume of LDHs.

The XRD patterns of Ca—Al—CO_3 LDH and its modified products are presented in Fig. 1 (A). The diffraction pattern of Ca—Al—CO_3 LDH (Fig. 1 A (a)) shows sharp and symmetric peaks at lower 2θ values (003 and 006), which are characteristic of LDH's crystalline structure (Ramírez-Llamas et al., 2015). These peaks disappeared after calcination (Fig. 1 A (b)) and microwave treatment (Fig. 1 A (c)), indicating the layered structure was destroyed, while an increase of the $Al(OH)_3$ and $CaCO_3$ peaks was observed (Sun et al., 2017). Upon re-hydration, the peaks of 003 and 006 are usually re-occurring (Ramírez-Llamas et al., 2015), underlining the recoverability of temperature-treated LDH materials. After aqueous F^- uptake, however, LDHs crystalline structure characteristic peaks (003 and 006) were not observed while characteristic peaks of $CaCO_3$ became stronger, indicating the LDHs crystalline structure was not rebuilt.

The FTIR spectra of Ca—Al—CO_3 LDH and its modified products are shown in Fig. 1 (B). The bands between 3600 and 3300 cm^{-1} are due to the vibrations of OH groups in the adjacent layers, the interlayer and/or adsorbed water (Noorjahan et al., 2015). The peaks at 1416 and 1362 cm^{-1} are due to the vibrations of sorbed CO_2 and interlamellar CO_3^{2-}, respectively (Lv et al., 2006; Cai et al., 2012). The bands between 1000 and 600 cm^{-1} can be attributed to characteristic vibrations of calcium and aluminum oxides (Lv et al., 2006; Das et al., 2003) (Fig. 1 B(a)). After calcination and microwave treatment, the vibrations of OH groups (3600-3300 cm^{-1}) mostly disappeared indicating the loss of water due to thermal treatment

Table 1
Overview of experimental conditions.

Experiment	F^- concentration (mg/L)	LDHs dose (g/L)	pH	Temp (°C)
Adsorption isotherm	2, 4, 6, 8, 10, 12	1	8	25 ± 1
Effect of temperature	10	1	8	12 ± 1, 25 ± 1, 35 ± 1
Adsorption kinetics	10	1	8	25 ± 1
Effect of co-existing anions	10	1	8	25 ± 1
Effect of dose	10	0.1, 0.2, 0.5, 1, 1.5, 2	8	25 ± 1
Effect of pH	10	1	6, 7, 8, 9, 10	25 ± 1

Table 2
Textural characteristics and pH_{pzc} of Ca—Al—CO_3 LDH and its modified products.

Sample	BET Surface Area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)	pH_{PZC}
Ca—Al—CO_3 LDHs	7.6	0.07	57.6	12.5
Calcined Ca—Al—CO_3 LDHs	7.1	0.10	66.6	12.3
Microwave treated Ca—Al—CO_3 LDHs	9.5	0.13	40.2	12.7

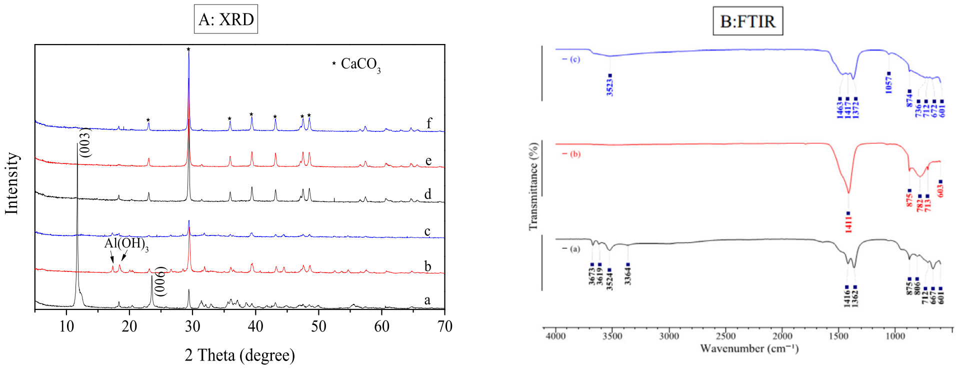

Fig. 1. XRD (A) and FTIR(B) spectra of Ca–Al–CO_3 LDHs (a), calcined Ca–Al–CO_3 LDHs (b) and microwave treated Ca–Al–CO_3 LDHs (c),Ca–Al–CO_3 LDHs after adsorption (d), calcined Ca–Al–CO_3 LDHs after adsorption (e) and microwave treated Ca–Al–CO_3 LDHs after adsorption (f); FTIR only measured before adsorption.

(Fig. 1 B(b)), which is in line with the XRD results. After calcination, the band at 1362 cm^{-1} disappeared and the band at 1416 cm^{-1} shifted to a lower frequency of 1411 cm^{-1} with a higher intensity indicating the loss of CO_3^{2-} species and the transformation of CO_3^{2-} to CO_2, which indicates that the layered structure of LDHs was destroyed by calcination, confirming the XRD findings.

3.2. F^- adsorption equilibrium

The adsorption isotherm results, given in Fig. 2, indicate that Ca–Al–CO_3 LDH and its modified products show affinity for F^- within the low initial F^- concentration range of 2–12 mg/L, up to F^- loadings of ~1% LDH weight. Although the differences are small, both modified LDHs exhibit a higher adsorption capacity than the raw LDH, especially at initial F^- concentrations >10 mg/L. However, it should be noted that both thermal treatments involve the loss of internal surface-bound water and calcination involves the loss of CO_3^{2-}, which do not occur when drying (105 °C) of the untreated LDH (cf. 3.1). Thus, the total mass of Ca–Al–CO_3 LDH added to the batches is somewhat higher for the calcined/microwave-treated LDHs, and consequently, the LDH-mass-related performance differences are smaller than those shown in Fig. 2. The isotherms are likely to be L-type curves without strict plateau (Limousin et al., 2007), however, the relatively low C_e range of the experiment restricts the curves to a mostly linear range.

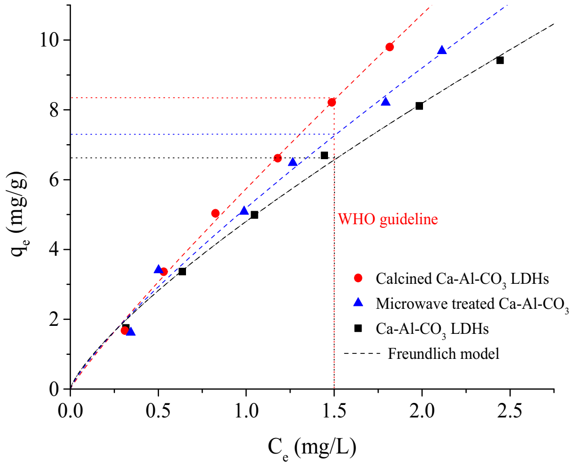

Fig. 2. F^- adsorption isotherm on Ca–Al–CO_3 LDH and its modified products, with loadings at WHO guideline of 1.5 mg/L value indicated as dashed lines. (Initial F^- = 2, 4, 6, 8, 10, 12 mg/L; pH = 8; adsorbent dose = 1 g/L; T = 25 ± 1 °C).

The fitting results indicate that Freundlich model can well fit the experimental data ($R^2 > 0.98$) (Table S1). At the C_e of 1.5 mg/L, the F^- adsorption capacities of calcined, microwave treated, and untreated Ca–Al–CO_3 LDHs are 8.4, 7.4, and 6.7 mg/g, respectively. For comparison, previous research has shown a F^- removal capacity of 1.84 mg/g for LDHs type Mg–Al–CO_3, at 5 mg/L (Wang et al., 2007). For Mg–Al–CO_3 LDH also higher capacities have been reported (319.8 mg/g), but these experiments were conducted at higher initial F^- concentrations (up to 2500 mg/L) (Lv et al., 2007).

The equilibrium isotherms of F^- uptake on Ca–Al–CO_3 LDH and its modified products at different temperatures (12 ± 1, 25 ± 1 and 35 ± 1 °C) are shown in Fig. 3. The F^- adsorption capacity of Ca–Al–CO_3 LDH and its modified products decreased with the increase in temperature, which indicates that F^- uptake on Ca–Al–CO_3 LDH and its modified products is an exothermic process (Errais et al., 2012).

3.3. F^- uptake kinetics

Fig. 4 shows the effect of contact time on F^- uptake by Ca–Al–CO_3 LDH and its modified products. For all Ca–Al–CO_3 LDH and its modified products, the F^- uptake increased rapidly during the initial 20 min, with a slower rate thereafter. Microwave treated and calcined Ca–Al–CO_3 LDHs present a higher F^- removal capacity than untreated Ca–Al–CO_3 LDHs. The experimental data fits to kinetic models are presented in the SI (pseudo first-order, pseudo-second-order, Elovich equation, and intraparticle diffusion, Fig. S2, Table S2), of which the pseudo second-order model resulted in the best data representation ($R^2 > 0.992$, Fig. S2b). The calculated adsorption capacity (q_e,cal) of Ca–Al–CO_3 LDHs, calcined Ca–Al–CO_3 LDHs and microwave treated Ca–Al–CO_3 LDHs was 6.38 mg/g, 7.18 mg/g and 7.22 mg/g, respectively, which are close to the experimental values (6.31, 7.09 and 7.16 mg/g, respectively). These values are lower than those obtained from Fig. 2 (~8 mg/g). A possible reason could be the acidification order, which was LDHs before acidification for the isotherm studies, while the opposite for the kinetic studies (same amount of acid dosed in both experimental series). As previously discussed, the thermal treatments might have resulted in an overestimation of the respective performances as compared to the raw LDH (cf. 3.2).

3.4. Effect of co-existing anions

Groundwater also contains common anions such as Cl^-, NO_3^-, HCO_3^-, SO_4^{2-}, potentially competing with F^- in adsorption (Kang et al., 2018). Especially the introduction of potentially competing anions by acidification (e.g. Cl^- by adding HCl) has been ignored in

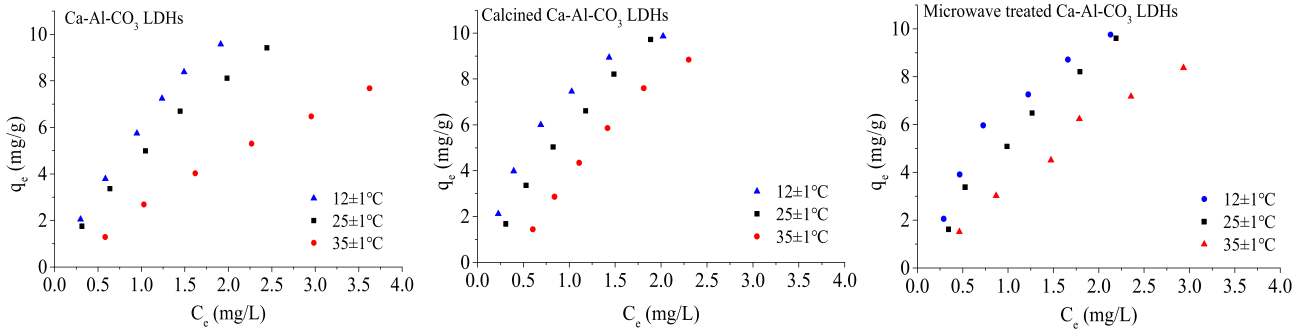

Fig. 3. Effect of temperature on the F^- removal by Ca–Al–CO_3 LDH and its modified products. (Initial F- = 2,4,6,8,10,12 mg/L; pH = 8; adsorbent dose = 1 g/L).

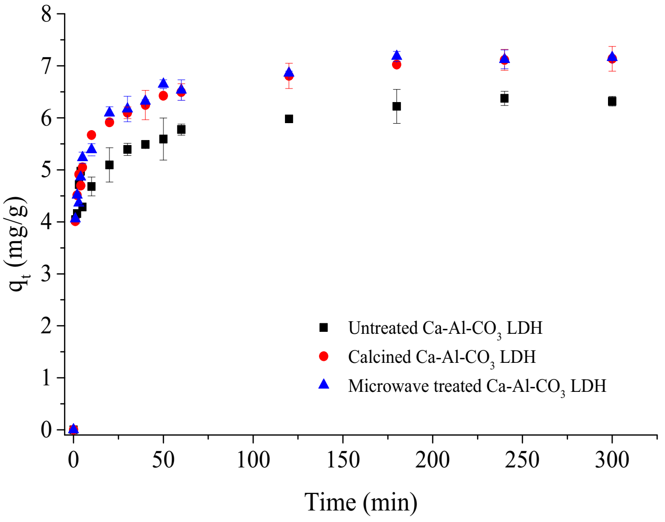

Fig. 4. The effect of contact time on F^- uptake by Ca–Al–CO_3 LDH and its modified products. (Initial F- = 10 mg/L; pH = 8; adsorbent dose = 1 g/L).

most previous studies. The impact of different anions on the defluorination performance of the unmodified LDH at variable doses is shown in Fig. 5. The data show that Cl^- and NO_3^- hardly affected the defluorination performance of Ca–Al–CO_3 LDHs, especially when their concentrations were lower than 100 mg/L. This observation is consistent with other findings for F^- removal by metal composite (Kang et al., 2018; Xiang et al., 2014; Wang et al., 2017; Tang and Zhang, 2016). One possible reason could be that chemical reactions (e.g. the formation of AlF_x complexes, precipitation of CaF_2) are involved in the removal process (Kang et al., 2018) and F^- has a stronger affinity for LDH adsorbents than Cl^- and NO_3^- (Tang and Zhang, 2016; Loganathan et al., 2013). At higher concentrations of 250 and 500 mg/L, HCO_3^- and SO_4^{2-} had a slight effect on the removal process. When the concentrations of HCO_3^- and SO_4^{2-} increased from 0 to 500 mg/L, the F^- removal percentage decreased from 83% to 71% and 77%, respectively. The weak effect of HCO_3^- and SO_4^{2-} at low concentrations (<100 mg/L) could be due to the large number of available adsorption sites. The stronger effect of HCO_3^- might be due to CO_3^{2-} in the interlayer of the LDH firstly being converted into HCO_3^-, then exchanged with F^-, but the presence of a high concentration of HCO_3^- potentially prevents the conversion process.

3.5. pH effect and buffering by LDHs

Ca–Al–CO_3 LDHs showed a noticeable effect on the pH of the solution. With the dose of 0.1–2 g/L, the unmodified Ca–Al–CO_3 LDH, and the calcined and microwave treated products increased the pH of the solution (from approximately 6.5) to 10.8–11.5, 10.1–11.6 and 10.8–11.7, respectively, indicating the release of hydroxyl ions from LDHs. In order to investigate the effect of adsorbent dose (and the corresponding pH effect) on F^- removal, the concentration of Ca–Al–CO_3 LDHs was varied from 0.1 g/L to 2 g/L with the initial F^-concentration of 10 mg/L, as presented in Fig. S3. The results clearly indicate that for all LDHs, with the increase in adsorbent dose, the adsorption capacity gradually decreased from around 30 mg/g to 5 mg/g (also corresponding to the data in Fig. 2). However, the F^- removal percentage considerably increased from 20% to 90% with the increase of adsorbent dose from 0.1 g/L to 2 g/L.

Fig. 6 shows the result of F^- uptake by Ca–Al–CO_3 LDH and its modified products over an initial pH range of 6–10. The Ca–Al–CO_3 LDH and its modified products presented a higher defluoridation capacity at a lower pH. A similar phenomenon was observed in other adsorbents, such as alumina (Viswanathan and Meenakshi, 2010), hydroxyapatite (Jiménez-Reyes and Solache-Ríos, 2010) and $KMnO_4$-modified activated carbon (Daifullah et al., 2007). One explanation is that the surface of adsorbents was positively charged with the decrease of pH due to their high pH_{pzc} (Table 2, Fig. S4) (Das et al., 2003). The pH_{pzc} of untreated, calcined and microwave treated Ca–Al–CO_3 LDHs were 12.5, 12.3 and 12.7, respectively. At pH below pH_{pzc}, the surface of the LDHs has a net positive charge which is favorable for F^- adsorption (Wu et al., 2015). This is due to the fact that hydroxyl groups on the surface (≡M) of LDHs were protonated at low pH and the sorption was dominated by the electrostatic interaction (Wu et al., 2017). The process could be expressed as follows (Kang et al., 2013):

$$\equiv MOH(s)H_2O \leftrightarrow \ \equiv MF(s) + H_2O \tag{2}$$

$$\equiv MOH_2^+(s) + F^-(aq) \leftrightarrow \ \ \equiv MF(s) + H_2O \tag{3}$$

In addition, at higher pH, more hydroxyl groups on the surface of LDHs could compete with F^- due to their similar ion radius (Feng et al., 2004).

The sharp increase in adsorption capacity when lowering the pH from 9 to 8 can potentially be explained by the HCO_3^-— CO_3^{2-} equilibrium. At pH 9, there is mainly CO_3^{2-} which is not beneficial for F^- removal because LDHs have a stronger affinity for divalent ions (e.g. CO_3^{2-}) than monovalent ions (e.g. F^-) (Lv et al., 2007). At pH 8, however, CO_3^{2-} converted to HCO_3^- which is beneficial for F^- removal. Although both HCO_3^- and F^- are monovalent, HCO_3^- only shows a slight reduction in F^- removal at high concentration (>250 mg/L) (Fig. 5). This hypothesis is supported by the finding that the pH effect is less prominent for the calcined Ca–Al–CO_3 LDHs (cf. Fig. 6), because its interlayered CO_3^{2-} was decomposed

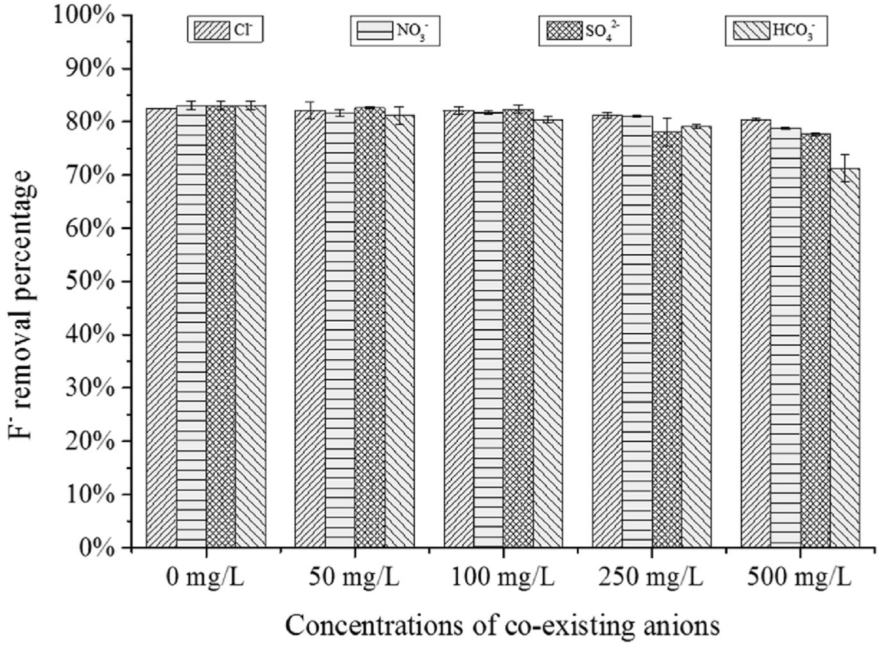

Fig. 5. Effect of co-existing anions on the F⁻ removal by unmodified Ca—Al—CO_3 LDH. (Initial F- = 10 mg/L; pH = 8; adsorbent dose = 1 g/L; T = 25 ± 1 °C).

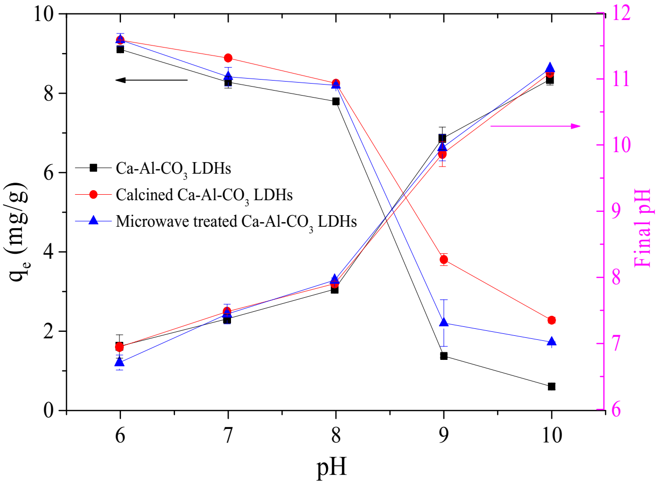

Fig. 6. Effect of initial pH on the F⁻ removal by Ca—Al—CO_3 LDH and its modified products. (Initial F- = 10 mg/L; pH = 6—10; adsorbent dose = 1 g/L; T = 25 ± 1 °C).

into CO_2 during the calcination (Ramírez-Llamas et al., 2015).

3.6. Discussion

Ca—Al—CO_3 LDHs are capable of removing F⁻ at environmentally-relevant concentrations with practically feasible LDH dosages. F⁻ removal capacities for untreated, calcined and microwave treated Ca—Al—CO_3 LDHs were similar, although XRD and FTIR spectra indicated (minor) changes to the LDH surface. The BET specific surface area of Ca—Al—CO_3 LDH and its modified products (<10 m^2/g) was lower than the surface areas obtained for Mg—Al—CO_3 LDHs (196.8 m^2/g) (Batistella et al., 2011), Zn—Al—Cl LDHs (92.6 m^2/g) (Mandal and Mayadevi, 2009), Zn—Cr—NO_3 LDHs (12—26 m^2/g) (Koilraj and Kannan, 2013) and Li—Al LDHs (37.24—51.27 m^2/g) (Tao et al., 2012). Nevertheless, the removal capacity was higher for Ca—Al—CO_3 LDHs compared to most other LDHs, i.e., 5 mg/g (initial F⁻ = 6 mg/L, pH = 8) for Ca—Al—CO_3 LDHs versus 1.84 mg/g (initial F⁻ = 5 mg/L, pH = 6) for Mg—Al—CO_3 LDHs (Wang et al., 2007) at similarly environmentally relevant F⁻ concentrations. This illustrates that F⁻ adsorption capacity of LDHs is not necessarily reflected in BET measurements with N_2, which may be explained by the fact the diameter of F⁻ (1.33 Å) (Shannon, 1976) is less than half the diameter of N_2 (3.64 Å) (Kentish et al., 2008). Also, although the removal of F⁻ by Ca—Al—CO_3 LDHs shown here appears promising, the exact pathway for F⁻ removal remains partly undisclosed. Both adsorption and anion exchange on the LDH surface might occur, but under specific conditions, also (surface) precipitation of $CaCO_3$ and/or $Al(OH)_3$ could occur (see XRD in Fig. 1A). The results of the PHREEQC calculations show that the precipitation of CaF_2 can occur at higher Ca^{2+} (>10 mg/L) and F⁻ (>4 mg/L) concentrations (Fig. S5). As such, $CaCO_3/Al(OH)_3$ precipitation processes on the surface of LDH cannot be excluded and could hypothetically contribute to F⁻ removal through enhanced adsorption. The pH dependency of F⁻ uptake by Ca—Al—CO_3 LDHs indicates that the CO_3^{2-}-HCO_3^- balance might be of importance to the F⁻ removal pathway and requires further investigation. For example, CO_3^{2-} in the interlayer of LDHs might be converted to HCO_3^-, making exchanges with F⁻ more favorable. While further studies on the exact removal pathway of F⁻ on Ca—Al—CO_3 LDHs are needed, this study has presented clear evidence that effective F⁻ removal is feasible in the lower concentration ranges as well as at practically applicable LDH dosages, and potential competition by other typical anions appears to be advantageously low.

For application it is, however, crucial to develop methods for granulation (e.g., by binding with sodium alginate, vinyl alcohol or a clay binder such as kaolin), as well as for pH control to achieve optimal performance. The strong buffering capacity of Ca—Al—CO_3 LDHs boosts the operating pH upwards (>pH 11), which is undesirable from a removal capacity perspective. Achieving lower operating pH (<pH 8) should be further examined, e.g. by pre-acidification of groundwater prior to LDH treatment. From an economic standpoint, at an F⁻ removal capacity of 6.7 mg/g, a kilogram of Ca—Al—CO_3 LDHs can treat about 788 L of F⁻ contaminated water (initial F⁻ = 10 mg/L; pH = 8; LDHs costs = € 3.8—5.2

per m^3 water; acidification costs = € 200.7 per m^3 water; for calculations refer to the SI), which is comparable to the widely applied active alumina (AA) whose limited defluorination capacity should be noted (normally <2 mg/g at neutral pH with initial F^- of 10 mg/L) (Mondal and George, 2015). In addition, the costs could be lower by using local raw materials (e.g. $CaCO_3$, $Ca(OH)_2$, $Al(OH)_3$) to synthesize LDHs. In combination with an environmentally friendly and cost-effective acidification method (e.g. aeration), Ca–Al–CO_3 LDH appears an attractive alternative for F^- removal.

4. Conclusions

Ca–Al–CO_3 LDHs, either untreated, calcined or microwave treated, showed affinity for the removal of F^- from synthetic groundwater in the environmentally-relevant lower concentration ranges (2–12 mg/L) to below the WHO guideline. F^- removal capacities at near-neutral pH were 6.7–8.4 mg F^-/g LDHs, with a higher capacity at lower pH (<8) and lower temperature (12 ± 1 °C). Defluorination capacity of Ca–Al–CO_3 LDHs is higher than that of Mg–Al LDHs ($q = 1.84$ mg/g, initial $F^- = 5$ mg/L, pH = 6) and active alumina (<2 mg/g at neutral pH with initial F^- of 10 mg/L) at similarly environmentally relevant F^- concentrations and the capacity is not necessarily reflected in BET measurements with N_2. Given only marginal defluorination improvements by calcination/microwave treatment, applying untreated LDH appears to be the practically most feasible option. Competition with Cl^- and NO_3^- was not observed, whereas at higher HCO_3^- and SO_4^{2-} concentrations (>250 mg/L), a slight reduction in F^- removal was observed. It is recommended to further investigate Ca–Al–CO_3 LDHs as a cost-effective F^- adsorbent with local raw materials, particularly in combination with pH correction to enhance its performance.

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Appendix A. Supplementary data

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References

Ayoob, S., Gupta, A.K., Bhat, V.T., 2008. A conceptual overview on sustainable technologies for the defluoridation of drinking water. Crit. Rev. Environ. Sci. Technol. 38, 401–470.
Batistella, L., Venquiaruto, L.D., Luccio, M.D., Oliveira, J.V., Pergher, S.B.C., Mazutti, M.A., Oliveira, D.B.D., Mossi, A.J., Treichel, H., Dallago, R.R., 2011. Evaluation of acid activation under the adsorption capacity of double layered hydroxides of Mg–Al–CO3 type for fluoride removal from aqueous medium. Ind. Eng. Chem. Res. 50, 6871–6876.
Benito, P., Labajos, F.M., Rives, V., 2009. Microwaves and layered double hydroxides: a smooth understanding. Pure Appl. Chem. 81, 1459–1471.
Bhatnagar, A., Kumar, E., Sillanpää, M., 2011. Fluoride removal from water by adsorption—a review. Chem. Eng. J. 171, 811–840.
Bhatnagar, A., Hogland, W., Marques, M., Sillanpää, M., 2013. An overview of the modification methods of activated carbon for its water treatment applications. Chem. Eng. J. 219, 499–511.
Cai, P., Zheng, H., Wang, C., Ma, H., Hu, J., Pu, Y., Liang, P., 2012. Competitive adsorption characteristics of fluoride and phosphate on calcined Mg–Al–CO3 layered double hydroxides. J. Hazard Mater. 213, 100–108.
Caporale, A., Pigna, M., Azam, S., Sommella, A., Rao, M., Violante, A., 2013. Effect of competing ligands on the sorption/desorption of arsenite on/from Mg–Fe layered double hydroxides (Mg–Fe-LDH). Chem. Eng. J. 225, 704–709.
Cavani, F., Trifiro, F., Vaccari, A., 1991. Hydrotalcite-type anionic clays: preparation, properties and applications, Catal. Today 11, 173–301.
Chang, Q., Zhu, L., Luo, Z., Lei, M., Zhang, S., Tang, H., 2011. Sono-assisted preparation of magnetic magnesium–aluminum layered double hydroxides and their application for removing fluoride. Ultrason. Sonochem. 18, 553–561.
Chitrakar, R., Sonoda, A., Makita, Y., Hirotsu, T., 2011. Calcined Mg–Al layered double hydroxides for uptake of trace levels of bromate from aqueous solution. Ind. Eng. Chem. Res. 50, 9280–9285.
Daifullah, A., Yakout, S., Elreefy, S., 2007. Adsorption of fluoride in aqueous solutions using KMnO4-modified activated carbon derived from steam pyrolysis of rice straw. J. Hazard Mater. 147, 633–643.
Das, D.P., Das, J., Parida, K., 2003. Physicochemical characterization and adsorption behavior of calcined Zn/Al hydrotalcite-like compound (HTlc) towards removal of fluoride from aqueous solution. J. Colloid Interface Sci. 261, 213–220.
Das, J., Patra, B., Baliarsingh, N., Parida, K., 2006. Adsorption of phosphate by layered double hydroxides in aqueous solutions. Appl. Clay Sci. 32, 252–260.
Dhiman, S., Keshari, A.K., 2006. Hydrogeochemical evaluation of high-fluoride groundwaters: a case study from Mehsana District, Gujarat, India. Hydrol. Sci. J. 51, 1149–1162.
Du, J., Sabatini, D.A., Butler, E.C., 2014. Synthesis, characterization, and evaluation of simple aluminum-based adsorbents for fluoride removal from drinking water. Chemosphere 101, 21–27.
Edmunds, W.M., Smedley, P.L., 2013. Fluoride in Natural Waters, Essentials of Medical Geology. Springer, Dordrecht, pp. 311–336.
Errais, E., Duplay, J., Elhabiri, M., Khodja, M., Ocampo, R., Baltenweck-Guyot, R., Darragi, F., 2012. Anionic RR120 dye adsorption onto raw clay: surface properties and adsorption mechanism. Colloids Surf., A 403, 69–78.
Feng, L., Zhang, L., Evans, D.G., Forano, C., Xue, D., 2004. Structure and thermal evolution of Mg–Al layered double hydroxide containing interlayer organic glyphosate anions. Thermochim. Acta 424, 15–23.
Ghorai, S., Pant, K., 2004. Investigations on the column performance of fluoride adsorption by activated alumina in a fixed-bed. Chem. Eng. J. 98, 165–173.
Ghosal, P.S., Gupta, A.K., 2015. An insight into thermodynamics of adsorptive removal of fluoride by calcined Ca–Al–(NO3) layered double hydroxide. RSC Adv. 5, 105889–105900.
Gupta, S.S., Bhattacharyya, K.G., 2011. Kinetics of adsorption of metal ions on inorganic materials: a review. Adv. Colloid Interface Sci. 162, 39–58.
Halajnia, A., Oustan, S., Najafi, N., Khataee, A., Lakzian, A., 2012. The adsorption characteristics of nitrate on Mg–Fe and Mg–Al layered double hydroxides in a simulated soil solution. Appl. Clay Sci. 70, 28–36.
Huang, L., Sun, Y., Wang, W., Yue, Q., Yang, T., 2011. Comparative study on characterization of activated carbons prepared by microwave and conventional heating methods and application in removal of oxytetracycline (OTC). Chem. Eng. J. 171, 1446–1453.
Ingram, L., Taylor, H., 1967. The crystal structures of sjögrenite and pyroaurite. Mineral. Mag. J. Mineral Soc. 36, 465–479.
Jiménez-Reyes, M., Solache-Ríos, M., 2010. Sorption behavior of fluoride ions from aqueous solutions by hydroxyapatite. J. Hazard Mater. 180, 297–302.
Kameda, T., Oba, J., Yoshioka, T., 2015. Kinetics and equilibrium studies on Mg–Al oxide for removal of fluoride in aqueous solution and its use in recycling. J. Environ. Manag. 156, 252–256.
Kang, D., Yu, X., Tong, S., Ge, M., Zuo, J., Cao, C., Song, W., 2013. Performance and mechanism of Mg/Fe layered double hydroxides for fluoride and arsenate removal from aqueous solution. Chem. Eng. J. 228, 731–740.
Kang, D., Yu, X., Ge, M., Lin, M., Yang, X., Jing, Y., 2018. Insights into adsorption mechanism for fluoride on cactus-like amorphous alumina oxide microspheres. Chem. Eng. J. 345, 252–259.
Kanno, C.M., Sanders, R.L., Flynn, S.M., Lessard, G., Myneni, S.C., 2014. Novel apatite-based sorbent for defluoridation: synthesis and sorption characteristics of nano-micro-crystalline hydroxyapatite-coated-limestone. Environ. Sci. Technol. 48, 5798–5807.
Kentish, S.E., Scholes, C.A., Stevens, G.W., 2008. Carbon dioxide separation through polymeric membrane systems for flue gas applications. Recent Pat. Chem. Eng. 1, 52–66.
Koilraj, P., Kannan, S., 2013. Aqueous fluoride removal using ZnCr layered double hydroxides and their polymeric composites: batch and column studies. Chem. Eng. J. 234, 406–415.
Lazaridis, N., Pandi, T., Matis, K., 2004. Chromium (VI) removal from aqueous solutions by Mg–Al–CO3 hydrotalcite: sorption–desorption kinetic and equilibrium studies. Ind. Eng. Chem. Res. 43, 2209–2215.
Li, F., Duan, X., 2006. Applications of Layered Double Hydroxides, Layered Double Hydroxides. Springer, Berlin Heidelberg, pp. 193–223.
Limousin, G., Gaudet, J.P., Charlet, L., Szenknect, S., Barthès, V., Krimissa, M., 2007. Sorption isotherms: a review on physical bases, modeling and measurement. Appl. Geochem. 22, 249–275.
Loganathan, P., Vigneswaran, S., Kandasamy, J., Naidu, R., 2013. Defluoridation of drinking water using adsorption processes. J. Hazard Mater. 248, 1–19.
Lv, L., 2007. Defluoridation of drinking water by calcined MgAl-CO3 layered double hydroxides. Desalination 208, 125–133.
Lv, L., He, J., Wei, M., Evans, D., Duan, X., 2006. Uptake of chloride ion from aqueous solution by calcined layered double hydroxides: equilibrium and kinetic studies. Water Res. 40, 735–743.
Lv, L., He, J., Wei, M., Evans, D., Zhou, Z., 2007. Treatment of high fluoride concentration water by MgAl-CO3 layered double hydroxides: kinetic and equilibrium studies. Water Res. 41, 1534–1542.
Lv, L., Sun, P., Gu, Z., Du, H., Pang, X., Tao, X., Xu, R., Xu, L., 2009. Removal of chloride

ion from aqueous solution by ZnAl-NO3 layered double hydroxides as anion-exchanger. J. Hazard Mater. 161, 1444–1449.

Ma, W., Zhao, N., Yang, G., Tian, L., Wang, R., 2011. Removal of fluoride ions from aqueous solution by the calcination product of Mg–Al–Fe hydrotalcite-like compound. Desalination 268, 20–26.

Mandal, S., Mayadevi, S., 2008. Adsorption of fluoride ions by Zn–Al layered double hydroxides, Appl. Clay Sci. 40, 54–62.

Mandal, S., Mayadevi, S., 2008. Cellulose supported layered double hydroxides for the adsorption of fluoride from aqueous solution. Chemosphere 72, 995–998.

Mandal, S., Mayadevi, S., 2009. Defluoridation of water using as-synthesized Zn/Al/Cl anionic clay adsorbent: equilibrium and regeneration studies. J. Hazard Mater. 167, 873–878.

Mohapatra, M., Anand, S., Mishra, B.K., Giles, D.E., Singh, P., 2009. Review of fluoride removal from drinking water. J. Environ. Manag. 91, 67–77.

Mondal, P., George, S., 2015. A review on adsorbents used for defluoridation of drinking water. Rev. Environ. Sci. Biotechnol. 14, 195–210.

Müller, G., Radke, C., Prausnitz, J., 1985. Adsorption of weak organic electrolytes from dilute aqueous solution onto activated carbon. Part I. Single-solute systems. J. Colloid Interface Sci. 103, 466–483.

Noorjahan, M., Khayyum, M., Mangatayaru, K.G., 2015. A novel cobalt modified layered double hydroxide for the efficient removal of fluoride. Mater. Focus 4, 283–289.

Osterwalder, L., Johnson, C.A., Yang, H., Johnston, R.B., 2014. Multi-criteria assessment of community-based fluoride-removal technologies for Rural Ethiopia. Sci. Total Environ. 532–538, 488-489.

Parkhurst, D.L., Appelo, C., 2013. Description of Input and Examples for PHREEQC Version 3: a Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. US Geological Survey.

Pérez, M., Pavlovic, I., Barriga, C., Cornejo, J., Hermosín, M., Ulibarri, M., 2006. Uptake of Cu2+, Cd2+ and Pb2+ on Zn–Al layered double hydroxide intercalated with edta. Appl. Clay Sci. 32, 245–251.

Ramírez-Llamas, L.A., Leyva-Ramos, R., Jacobo-Azuara, A., Martínez-Rosales, J.M., Isaacs-Paez, E.D., 2015. Adsorption of fluoride from aqueous solution on calcined and uncalcined layered double hydroxide. Adsorpt. Sci. Technol. 33, 393–410.

Shannon, R.D., 1976. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr. - Sect. A Cryst. Phys. Diffr. Theor. Gen. Crystallogr. 32, 751–767.

Sun, Z., Park, J.-S., Kim, D., Shin, C.-H., Zhang, W., Wang, R., Rao, P., 2017. Synthesis and adsorption properties of Ca-Al layered double hydroxides for the removal of aqueous fluoride. Water Air Soil Pollut. 228, 23.

Tang, D., Zhang, G., 2016. Efficient removal of fluoride by hierarchical Ce–Fe bimetal oxides adsorbent: thermodynamics, kinetics and mechanism. Chem. Eng. J. 283, 721–729.

Tao, Z., Li, Q., Xiao, H., Lu, H., Zhou, Y., 2012. Synthesis of Li–Al layered double hydroxides (LDHs) for efficient fluoride removal. Ind. Eng. Chem. Res. 51, 11490–11498.

Viswanathan, N., Meenakshi, S., 2010. Enriched fluoride sorption using alumina/chitosan composite. J. Hazard Mater. 178, 226–232.

Wang, H., Chen, J., Cai, Y., Ji, J., Liu, L., Teng, H.H., 2007. Defluoridation of drinking water by Mg/Al hydrotalcite-like compounds and their calcined products. Appl. Clay Sci. 35, 59–66.

Wang, M., Yu, X., Yang, C., Yang, X., Lin, M., Guan, L., Ge, M., 2017. Removal of fluoride from aqueous solution by Mg-Al-Zr triple-metal composite. Chem. Eng. J. 322, 246–253.

Wen, D., Zhang, F., Zhang, E., Wang, C., Han, S., Zheng, Y., 2013. Arsenic, fluoride and iodine in groundwater of China. J. Geochem. Explor. 135, 1–21.

World Health Organization, 2004. Guidelines for Drinking-Water Quality: Recommendations. World Health Organization.

Wu, T., Mao, L., Wang, H., 2015. Adsorption of fluoride on Mg/Fe layered double hydroxides material prepared via hydrothermal process. RSC Adv. 5, 23246–23254.

Wu, H., Zhang, H., Yang, Q., Wang, D., Zhang, W., Yang, X., 2017. Calcined chitosan-supported layered double hydroxides: an efficient and recyclable adsorbent for the removal of fluoride from an aqueous solution. Materials 10, 1320.

Xiang, W., Zhang, G., Zhang, Y., Tang, D., Wang, J., 2014. Synthesis and characterization of cotton-like Ca–Al–La composite as an adsorbent for fluoride removal. Chem. Eng. J. 250, 423–430.

Yuen, F.K., Hameed, B., 2009. Recent developments in the preparation and regeneration of activated carbons by microwaves. Adv. Colloid Interface Sci. 149, 19–27.

Zhang, T., Li, Q., Xiao, H., Mei, Z., Lu, H., Zhou, Y., 2013. Enhanced fluoride removal from water by non-thermal plasma modified CeO2/Mg–Fe layered double hydroxides. Appl. Clay Sci. 72, 117–123.