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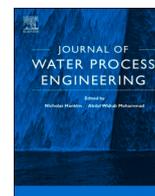Wei, Liangfu; Zietzschmann, Frederik; Rietveld, Luuk C.; van Halem, Doris

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Fluoride removal from water by Ca-Al-CO$_3$ layered double hydroxides and simultaneous acidification

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ABSTRACT

Millions of people worldwide are exposed to excessive concentrations of fluoride (F$^-$) from groundwater sources. Ca-Al-CO$_3$ layered double hydroxides (LDHs) have shown promising defluoridation efficiency; however, defluoridation by Ca-Al-CO$_3$ LDHs is highly pH sensitive. This study showed that simultaneous acidification by conventional acids, such as HCl and CO$_2$ substantially increased the performance of Ca-Al-CO$_3$ LDHs for F- removal at environmentally relevant concentrations (e.g., 10 mg/L) to below the WHO guideline value (1.5 mg/L), while, in comparison to other acids (HNO$_3$, H$_2$SO$_4$, H$_3$PO$_4$), the use of HCl and CO$_2$ does not lead to the introduction of potentially harmful or undesired anions. The addition of HCl and CO$_2$ to LDHs suspensions did lead to changes to the LDHs structure. Leaching experiments, supported by PHREEQC modelling and characterization (SEM-EDX, XRD and FTIR), strongly suggest that the main mechanism of F- removal by Ca-Al-CO$_3$ LDHs was F$^-$ adsorption or complexation onto/into various rehydrated mixed metal oxides which re-precipitated upon partial LDHs dissolution when acidifying.

1. Introduction

Fluoride (F$^-$) is a trace element that plays a crucial role in the prevention and control of dental caries [1], however, exposure to excessive F$^-$ concentrations can lead to dental and skeletal fluorosis [2]. Over 200 million people worldwide are exposed to excessive concentrations of F$^-$ from groundwater sources [3]. India and China are the worst affected, around 67 million and 41 million people are affected by fluorosis, respectively [4]. In the past decades, numerous methods (e.g., adsorption, ion exchange, electrochemical, coagulation, and membrane processes,) and materials (e.g., activated alumina, bone char, synthetic hydroxyapatite, biosorbents) have been investigated for F$^-$ removal [5, 6]. However, a sustainable solution to this ongoing crisis still appears intangible due to various obstacles, including removal efficiency, material costs, social acceptability, complexity of operation and maintenance [7].

Layered double hydroxides (LDHs) are a family of anionic clays that have attracted considerable attention and are considered applicable in F$^-$ removal due to their high defluoridation capacity and cost-effectiveness [8]. The general formula of LDHs can be expressed as $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} [A^{m-}_{x/m} \cdot nH_2O]$, where M^{2+} and M^{3+} correspond to a divalent and trivalent metal, respectively, where A^{m-} is an

exchangeable anion [9,10]. Various kinds of LDHs such as Mg-Al, Zn-Al, Ni-Al, Li-Al, Mg-Cr, Mg-Fe, Fe-Mg-Al LDHs, have been studied for F-removal from aqueous solutions [9,11–16]. Among these LDHs types, the most studied are the Mg-Al LDHs and their calcined products, which are of particular value at higher F- concentration ranges. In contrast, F-removal by Ca-Al LDHs is rarely reported, but considering the affinity of Ca^{2+} and Al^{3+} towards F- [17], has recently shown promising defluoridation efficiency at low, environmentally relevant F- concentrations (2−12 mg/L) [18] (Table 1). However, defluoridation by Ca-Al-CO$_3$ LDHs is highly pH sensitive, with better removals at pH 6–8 compared to ≥ pH 9, with the inherent problem of Ca-Al-CO$_3$ LDHs to react caustic upon addition to water (i.e., pH of point of zero charge 12–13), resulting in reduced defluoridation (~5%, pH = 11.5, initial F$^-$ = 10 mg/L) [18].

As a consequence, acidification is required, e.g. by hydrochloric acid (HCl), nitric acid (HNO$_3$) [22–25], or CO$_2$ [7,26]. However, potential effects of such acidification on Ca-Al-CO$_3$ LDHs-induced F- removal and associated impacts on the water matrix have not been studied previously, despite being mentioned as problematic and potentially hampering successful application. The mechanism of F- removal by LDHs was mainly explained as F- adsorption and anion exchange [13, 14]. Considering the structural properties and the adsorption/ion exchange characteristics of LDHs, more examinations are needed to

Table 1
Comparison of F$^-$ removal capacities by different LDHs at environmentally relevant concentrations.

Type of LDHs	Dosage (g/L)	F$^-$ Initial concentration(mg/L)	pH	F$^-$ removal capacity (mg/g)	References
Ca-Al-CO$_3$	1	10	6	9.1	[18]
Mg-Al-CO$_3$	1.11	10	6	7.63[a]	[19]
Ni-Al-NO$_3$	2	10	6	4.82[a]	[20]
Zn-Al-Cl	4	10.2	6.2	1.9	[21]
Mg-Al-CO$_3$	2.5	5	6	1.84	[16]

[a] Kinetic model (Pseudo-second-order) value.

understand the possible negative impacts of applying Ca-Al-CO$_3$ LDHs in combination with acidification such as increased anion concentrations, competitive adsorption, and modifications/changes to the structure of Ca-Al-CO$_3$ LDHs, to further explore the mechanism of F- removal. Therefore, the main objectives of this study were to a) elucidate and compare the impact of various pH-adjusting acids on F- removal by Ca-Al-CO$_3$ LDHs from water at environmentally relevant F- concentrations; b) examine the associated effects on the LDHs material and water composition; c) propose the main mechanism of F- removal by Ca-Al-CO$_3$ LDHs.

2. Materials and methods

2.1. Chemicals and materials

All reagents including NaF, HCl, HNO$_3$, H$_2$SO$_4$, and H$_3$PO$_4$ used for the experiments were of analytical grade (Sigma-Aldrich). All the water used throughout the experiments and treatment processes was lab-produced deionized water. An F$^-$ stock solution (1000 mg/L) was prepared with NaF and then diluted to the desired concentrations. The used Ca-Al-CO$_3$ LDHs (ACTILOX®CAHC) were of a Ca$_4$Al$_2$(OH)$_{12}$CO$_3$·nH$_2$O (n = 4–5) type, with a Ca/Al ratio of 1.86, obtained from Nabaltec (Germany). Ca-Al-CO$_3$ LDHs were dried in an oven at 105 °C for 12 h before use to get rid of water that may be adsorbed.

2.2. Batch experiments and kinetic studies

An overview on the conducted experiments is given in Fig. 1. For
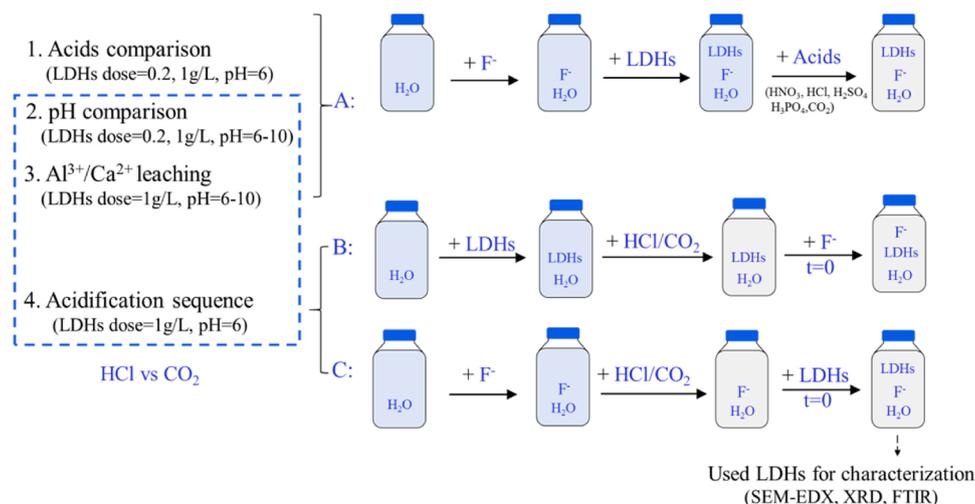
acids comparison, Ca-Al-CO$_3$ LDHs samples (0.02 or 0.1 g) were firstly dispersed in 100 mL NaF solution (10 mg F$^-$/L), directly followed by acidification to pH 6 (within ~15 min) using various acids (1 M HCl, 1 M HNO$_3$, 0.5 M H$_2$SO$_4$, 0.33 M H$_3$PO$_4$) or by injection of CO$_2$ with a flow of 5 mL/min (10 min), respectively (acid doses recorded), and stirring for 24 h (enough to reach equilibrium based on previous studies [14,18]) with subsequent pH measurement and membrane filtration by 0.45 μm to remove the solids. In a similar manner, different pHs (6, 7, 8, 9, 10) were compared at an initial F$^-$ concentration of 10 mg/L (100 mL), as well as effects of different LDHs' doses (0.1, 0.15, 0.2, 0.5, 1, 2 g/L) at pH 6 (cf. supplementary materials (Figure S1)). Ca^{2+} and Al^{3+} leaching were examined afterwards, and, to minimize potential impacts of Al-species smaller than the membrane pore size (0.1 μm), the samples were centrifuged at 10,000 rpm for 10 min prior to filtration. Effects of variable F- concentration on the overall removal efficiency were tested at pH 6, 0.2 g Ca-Al-CO$_3$ LDHs, 100 mL, and initial F$^-$ of 2, 4, 6, 8, 10, 12 mg/L (cf. supplementary materials). In kinetic studies ("acidification sequence", cf. Fig. 1), pH was adjusted to 6 by both HCl and CO$_2$ after 1 g/L LDHs addition, followed by F$^-$ dosage of 10 mg F-/L (cf. "B" in Fig. 1), and F- was dosed to 10 mg F-/L, followed by acidification (same dosage as in "B") and 1 g/L LDHs addition (cf. "C" in Fig. 1). The solutions were stirred for 3 h under pH 6 with a cap on the jars (1 L) to avoid the influence of air, samples of 3 mL each were collected and filtered (0.45 μm) after 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150 and 180 min, respectively. Solid material samples were obtained by 0.1 μm filtration at the end of the kinetic experiments, and dried in an oven at 105 °C for 12 h, then cooled and ground into powder for further use.

2.3. Analytical methods

Scanning electron microscope (SEM) images and X-ray analyses (EDX) of Ca-Al-CO$_3$ LDHs samples before and after F$^-$ removal were taken on a JEOL scanning electron microscope (JSM-IT100). The functional groups in samples were determined from fourier transform infrared spectroscopy (FTIR) spectra by a fourier transform infrared spectrometer (Spectrum TM 100 Optical ATR-FTIR), following pelletization of the materials. The crystalline structure of the samples was characterized using an X-ray Bruker D8 Advance diffractometer (Bruker).

The concentrations of F$^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$ and HCO$_3^-$ were analyzed by Ion chromatography (IC) (Metrohm 881, Switzerland) with a column of Mestrosep A Supp 5 and ICE-99-9860, respectively. Concentrations of Ca^{2+} and Al^{3+} leaching after experiment were measured by ICP-MS (Analytik Jena AG, Germany).

Fig. 1. Overview of experimental conditions and procedures.

2.4. Data evaluation and modelling

The F⁻ removal efficiency (%) at equilibrium and non-equilibrium contact times was calculated using the following formula:

$$F^- \text{ removal efficiency} = \frac{(C_0 - C)}{C_0} \times 100\% \tag{1}$$

where C_0 and C are initial and F⁻ concentrations (mg/L) at equilibrium and non-equilibrium contact times, respectively. Data evaluation and model fitting to experimental data were accomplished using OriginPro 9.0. The calculation of saturation index (SI) of CaF_2 and the distribution of Al and Ca species was carried out using PHREEQC [27,28]. Detailed descriptions of simulation and input files can be found in the supplementary information (cf. Section 4).

3. Results and discussion

3.1. Comparison of acidification by various acids

The F⁻ removal by Ca-Al-CO₃ LDHs at 0.2 and 1 g/L from solutions adjusted to pH 6 by acidification with various acids are shown in Fig. 2A. A dosage of 0.2 g/L was chosen to reach well-discernible results, which is comparatively lower than previous studies on LDHs (0.5–7.5 g/L) [14, 29,30], and much lower than that on Indian Bauxite (12−77 g/L) [7]. A pH of 6 was chosen to reach well-discernible results and because substantial benefits of lower pH were observed previously [14,18,30]. Under acidified conditions the removal reached 37% (CO₂) and 64% (HCl) at a 0.2 g/L LDHs dose, 90% (CO₂) and 94% (HCl) at 1 g/L LDHs. At the lower LDHs dose, acidification by HNO₃ resulted in a similar F⁻ removal as HCl, whereas for H₃PO₄, H₂SO₄, removals were 5 and 8 % lower, respectively, possibly due to increased competition of PO_4^{3-} and SO_4^{2-} with F- because of their electrostatic interaction, as compared to Cl- and NO₃- [24]. At the higher LDHs dose of 1 g/L, F- removal differences between the tested acidification methods were small and seemed to remain unchanged at different initial concentrations of F-, due to overall high removal ≥90%.

The high pH buffering capacity of Ca-Al-CO₃ LDHs caused the solution pH to rise to 10.9–11.5 at LDHs doses of 0.2 and 1 g/L, but better F⁻ removals were obtained at lower pH. Therefore, to reach the intended pH (6), considerable dosages of acids were required after LDHs addition. At LDHs dose of 1 g/L, the addition of HCl (∼478 mg/L) is similar to the report by Cherukumilli et al. (211−401 mg/L) while the addition of CO₂ (∼0.99 g/L) is much lower than the reports by Cherukumilli et al. (22.5−34.7 g/L) [7] and Li et al. (80.1 g/L) [26], although the amount of acids is usually not reported [22–25]. The consequent anion concentrations (Cl-, NO₃-, PO_4^{3-}, SO_4^{2-} and HCO₃–) at 1 g/L LDHs are given in Fig. 2B, at the start and end of the experiments, respectively. The consequent concentrations of NO₃-, SO_4^{2-} and PO_4^{3-} were much higher

than the drinking water threshold (cf. Table S3), whereas the concentrations of Cl- and HCO₃- were thought to be acceptable because although excessive Cl- concentrations (> 250 mg/L) is detectable by taste, a guideline value for Cl- in drinking water is not established, and HCO₃- is not proposed as a chemical related to taste or odour in drinking water [31,32]. The NO₃- concentration, after dosing HNO₃, was 835 mg/L and decreased only slightly during the experiments (829 mg/L). At lower Ca-Al-CO₃ LDHs dose (0.2 g/L), NO₃- concentration was still high (∼170 mg/L). The PO_4^{3-} concentrations, after dosing H₃PO₄, decreased from 795 to 238 mg/L during the experiments, and SO_4^{2-} concentrations, after dosing H₂SO₄, decreased from 671 to 618 mg/L. These results indicate a partial uptake of PO_4^{3-} and SO_4^{2-} by Ca-Al-CO₃ LDHs and could potentially result in competition between F- and PO_4^{3-} or SO_4^{2-}, as LDHs have been previously documented to have a stronger affinity for multivalent anions [14], then for monovalent ions. The high uptake of PO_4^{3-} could also be due to the formation of Ca-PO₄ precipitate (SI of Hydroxyapatite = 6.31 calculated by PHREEQC at pH6) under such condition [33]. HCl acidification resulted in ∼450 mg/L Cl- and the concentration of introduced HCO₃-, after dosing CO₂, was approximately 550 mg/L at 1 g/L LDHs.

3.2. Effect of pH and initial F- concentration on F- removal

While considerable differences were not discernible between HCl and CO₂ acidification at the high LDHs dose, F⁻ removal was slightly higher for HCl than for CO₂ at the lower LDHs doses at pH 6 and 7; at higher pH, no differences appeared (Fig. 3A). Overall, F⁻ removal increased with decreasing pH, and the effect was more pronounced for HCl than for CO₂ acidification, possibly due to competition by HCO₃⁻. Upon application of CO₂, HCO₃⁻ concentrations rose to 550 mg/L and 168 mg/L at pH 6 and 7, respectively, which is higher than for HCl (< 90 mg/L, because of the dissolution of LDHs). Earlier research has indicated a slight reduction in F⁻ removal due to elevated HCO₃- concentrations (>250 mg/L); such an adverse effect was not observed for Cl⁻ as a competitive anion [18].

The F⁻ removal by 0.2 and 1 g/L Ca-Al-CO₃ LDHs at varying initial F-concentrations are shown in Fig. 3B. The F- removal decreased gradually with the increase of initial F- concentrations at 0.2 g/L LDHs; for 1 g/L LDHs, the initial F- concentration has little discernible effect. Independent of the initial F⁻ concentration, higher F- removal was reached when acidifying with HCl than when using CO₂, especially at the lower LDHs dose (0.2 g/L), likely confirming potential adverse competitive effects of HCO₃- (cf. 3.1). At the Ca-Al-CO₃ LDHs dose of 0.2 g/L, concentration of, approximately, 6 mg/L and 3.8 mg/L of F⁻ could be reduced when pH was adjusted by HCl and CO₂, respectively, whereas all the initial concentrations, 2−12 mg F⁻/L, were reduced to below WHO guideline (1.5 mg/L) at the Ca-Al-CO₃ LDHs dose of 1 g/L (Figure S4).
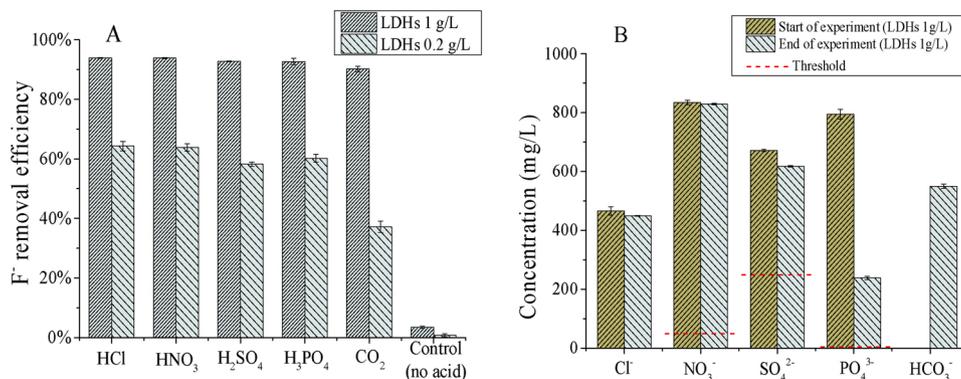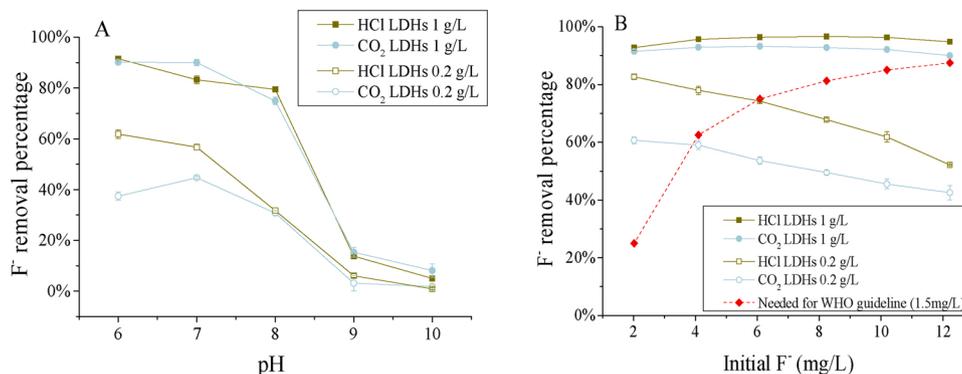

Fig. 2. (A) F⁻ removal efficiency at 0.2 and 1 mg/L LDHs dose, and (B) anion concentration of different pH-adjusting acids at start and end of the experiment. Initial F- = 10 mg/L, initial pH = 6, T = 22 ± 1℃, LDHs dose = 0.2 or 1 g/L.

**Fig. 3.** The effect of pH (A) (Initial $F^- = 10$ mg/L; pH = 6, 7, 8, 9, 10; LDHs dose = 0.2 g/L; T = 22 ± 1℃) and initial F^- (B) (LDHs Initial F^- = 24,681,012 mg/L; pH = 6; LDHs dose = 0.2 or 1 g/L; T = 22 ± 1℃) on F^- removal by Ca-Al−CO_3.

3.3. Effect of acidification sequence on F^- removal

In order to better understand the F^- removal process, two groups of experiments were carried out to investigate the effect of time and acidification order. F- was dosed either after or before acidification of the Ca-Al-CO_3 LDHs-containing suspension (cf. Fig. 1). The absolute and relative F- removal is depicted over time for the two tested acidification orders with HCl and CO_2, respectively, in Fig. 4. Several models fit to the kinetic experimental data and are presented in the supplementary information. HCl acidification resulted in faster removal kinetics than CO_2 acidification. Specifically, equilibria were reached after 20 min, 60 min, 90 min, >180 min for HCl + F- before/after and CO_2 + F- before/after, respectively. Thus, the F- removal performance was overall faster when LDHs were added to solutions already containing F- and acid, as compared to when F- was dosed to suspensions previously containing acidified LDHs.

Potentially, the Ca-Al-CO_3 LDHs surfaces were firstly activated by acids when acidified (prior to F^- addition) and simultaneously occupied by respective anions (Cl^- and HCO_3^-), which subsequently had to be replaced when F^- was added. The effect was particularly pronounced for CO_2, where the F^- removal during F^- dosage after acidification only approached the removal during F^- dosage before acidification after several hours. Possibly, the competition for adsorption sites between F^- and HCO_3^- were more pronounced than with the other ions. When CO_2 is diffusing into the solution, the hydration of CO_2 can occur in two paths. At pH > 10, the predominant mechanism is via direct reaction with OH^- forming HCO_3^- and CO_3^{2-} (instantaneous); At pH < 8, the direct hydration is the predominant mechanism forming H_2CO_3 and HCO_3^-
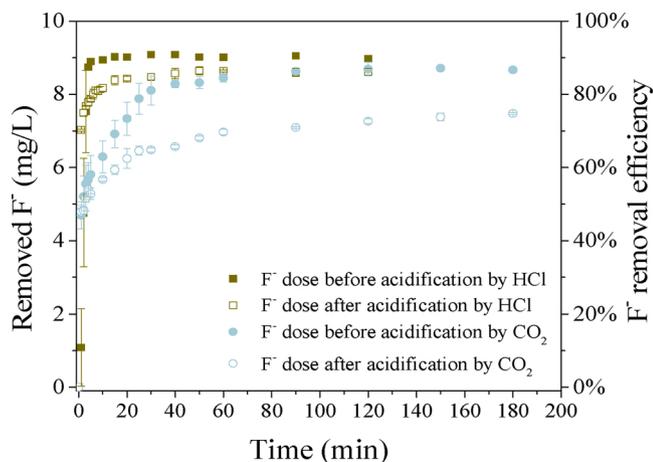
(instantaneous) [34,35] and resulting in a high concentration of HCO_3^- which has an adverse effect on F- removal [18]. During HCl acidification there was little difference between dosage of F^- before or after acidification (similar equilibrium removal). Apparently Cl^- had little competition with F^-. Although < 90 mg/L of HCO_3^- can be formed because of the dissolution of LDHs after HCl acidification, no adverse effect was observed at this concentration [18].

3.4. Al^{3+} and Ca^{2+} leaching

Fig. 5 shows the Al^{3+} and Ca^{2+} concentrations after addition of 1 g/L Ca-Al-CO_3 LDHs. The concentration reached ~70 mg/L for both Al^{3+} and Ca^{2+} without pH control (pH = 11.5). After HCl acidification, Al^{3+} concentrations ranged between 0.05 mg/L (pH 6) and 75 mg/L (pH 10) and Ca^{2+} concentrations ranged between 184 mg/L (pH 9) and 273 mg/L (pH 6). During CO_2 acidification, Al^{3+} concentrations were in the range of 0.12 mg/L (pH 6) to 54 mg/L (pH 10), and Ca^{2+} ranged from 35 mg/L (pH 9) to 241 mg/L (pH 6). CO_2 acidification thus caused slightly higher Al^{3+} leaching at pH below 9 but less Ca^{2+} leaching compared to HCl. Ca^{2+} concentrations were within the ranges of the WHO (100−300 mg/L), however, occasionally additional Ca^{2+} removal could be needed if this water is distributed for drinking water supply (World Health Organization, 2011). The observed Al^{3+} and Ca^{2+} leaching indicates the dissolution of Ca-Al-CO_3 LDHs. Based on its formula $Ca_4Al_2(OH)_{12}CO_3 \cdot nH_2O$ (n = 4–5) and the measured concentrations of Ca^{2+}, approximately 24% of Ca-Al-CO_3 LDHs was dissolved with no pH control and over 94% (273 mg/L) and 83% (241 mg/L) dissolved at pH 6 for HCl and CO_2 acidification, respectively.

3.5. Proposed removal mechanism

Given the reduced Al^{3+} concentrations at decreased pH, it is likely that Al-containing precipitates were formed from the previously dissolved LDHs. Composition, structure and morphology of precipitated Al species are affected by pH value, from a pure bayerite phase through bayerite (α-Al(OH)$_3$) and boemhite (γ-AlOOH) to amorphous Al species with decreasing pH from 11 to 6 [36]. F^- removal from solution onto such precipitates was previously observed [37,38].

The distribution of Al and F species under varying pH conditions was simulated by PHREEQC based on the found leaching concentrations, as shown in Fig. 6. For the Al species distribution, $Al(OH)_4^-$ accounted for ~8 % at pH 6, ~70% at pH 7, and >99% for pH > 8. The predominant species at pH 6 was $Al(OH)_2^+$ (~32%), followed by AlF^{2+} (~23%) and AlF_2^+ (~22%). For the F species distribution, free F- was ~0.3% at pH 6, ~10% at pH 7, and >94% at pH > 8. AlF^{2+} (~55%) and AlF_2^+ (~44%) were two predominant species at pH 6.

PHREEQC modelling (cf. Figures S5, S6) underlined that CaF_2 precipitation was strongly hampered by Al^{3+} presence, indicating that the here observed F^- removal resulted rather from F/Al interactions than
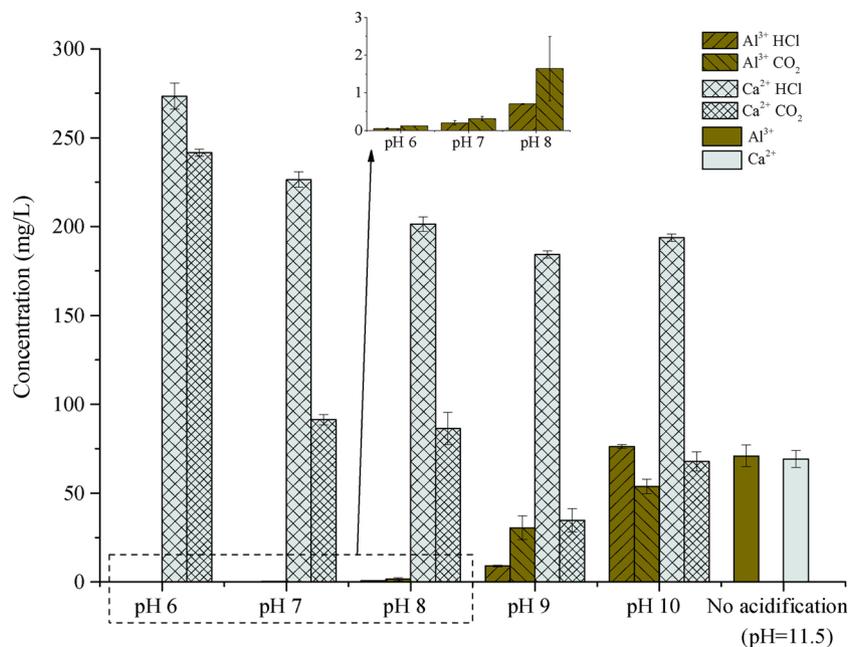

Fig. 4. F^- removal capacity and removal percentage, as a function of time. Initial F- = 10 mg/L; pH = 6; LDHs dose = 1 g/L; T = 22 ± 1℃.

Fig. 5. Al^{3+} and Ca^{2+} leaching from Ca-Al−CO_3 LDHs under different pH conditions; inset: Al^{3+} concentrations for pH 6, 7, 8. Initial $F^- = 10$ mg/L, T $= 22 \pm 1$℃, LDHs dose $= 1$ g/L.
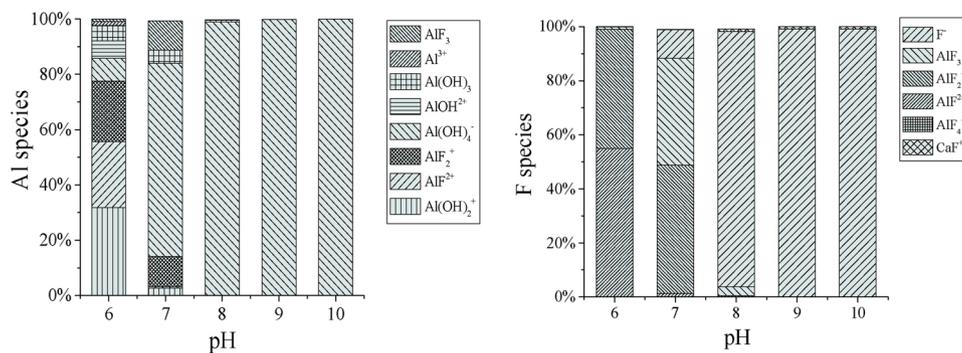
Fig. 6. Distribution of Al and F species under different pH conditions simulated by PHREEQC. T $= 25$℃, pH $= 6$-10, $F^- = 10$ mg/L, the molar ratio of $F^-/Al^{3+} = 0.2$.

from F/Ca. According to PHREEQC modelling and literature data, the various Al-containing species such as $Al(OH)_2^+$, AlF^{2+}, AlF_2^+, $Al(OH)_4^-$, etc. were present under the tested conditions, particularly when lowering the pH < 8, likely serving as adsorption/complexation/interaction partners for F^-, depending on the respective pH and F^-/Al^{3+} ratio [39–41] (Fig. 7). But specifically for CO_2 acidification, F^- can also be removed by $CaCO_3$ adsorption [42]. The pH buffering capacity of Ca-Al-CO_3 LDHs played a positive impact on F- removal by fully hydrolyzing Al^{3+} before Al-F complexation.

3.6. Characterization of Ca-Al-CO₃ LDHs before and after use

Given the observed dissolution and re-precipitation of the tested Ca-Al-CO_3 LDHs, morphology and structure, before and after experiments (cf. "C" in Fig. 1), were further characterized. The SEM-EDX results in Figure S7 show a reduction of Ca, particularly for acidification by HCl, confirming the observed leaching of this cation. The formed HCO_3^- after CO_2 acidification (~550 mg/L) is much more than that after HCl acidification (<90 mg/L), which likely inhibited the dissolution of $CaCO_3$ (cf. Figure S6). EDX further shows presence of F- after the experiments, thus verifying F^- uptake into solids for both acidification methods. XRD patterns of Ca-Al-CO_3 LDHs before and after the experiments are given in Fig. 8A. The virgin LDHs show sharp and symmetric characteristic

peaks (003 and 006) of hydrotalcite-like compounds at lower 2Theta values [43], which almost disappeared by both tested acidification methods, indicating the damage of the layered hydrotalcite-like structure, different from previously examined with Mg-Al type LDHs [13,29, 44]. The phase identification shows that the Ca-Al-CO_3 LDHs after HCl acidification were amorphous, whereas after CO_2 acidification the main compounds were $CaCO_3$ and $Al(OH)_3$. The aqueous stability of LDHs is driven by the solubility of the corresponding divalent metal salt [45,46]. The damage of the layered hydrotalcite-like structure after acidification indicated a low stability of Ca-Al-CO_3 LDHs.

The FTIR spectra of Ca-Al-CO_3 LDHs before and after the experiments are shown in Fig. 8B. Acidification by HCl led to profound structural changes, as indicated by the disappearance of nearly all bands (OH groups in brucite-like layers, interlayer and/or adsorbed water at $3600-3300$ cm^{-1} [47], sorbed CO_2 and interlamellar CO_3^{2-} at 1419 and 1363 cm^{-1} [29,48], as well as calcium and aluminum oxides at 1000 and 600 cm^{-1} [30,48]). Structural changes by CO_2 acidification were less severe, mainly impacting the layered hydrotalcite-like structure (disappearance of bands between 3600 and 3300 cm^{-1}). The high concentration of HCO3- resulting from the CO_2 injection likely inhibited the dissolution of $CaCO_3$ (cf. Figure S6) and probably led to the formation of $Al(OH)_3$ due to the weak acid property of H_2CO_3 [49]. Adsorbents with a high defluoridation capacity are often double or triple metal oxides,
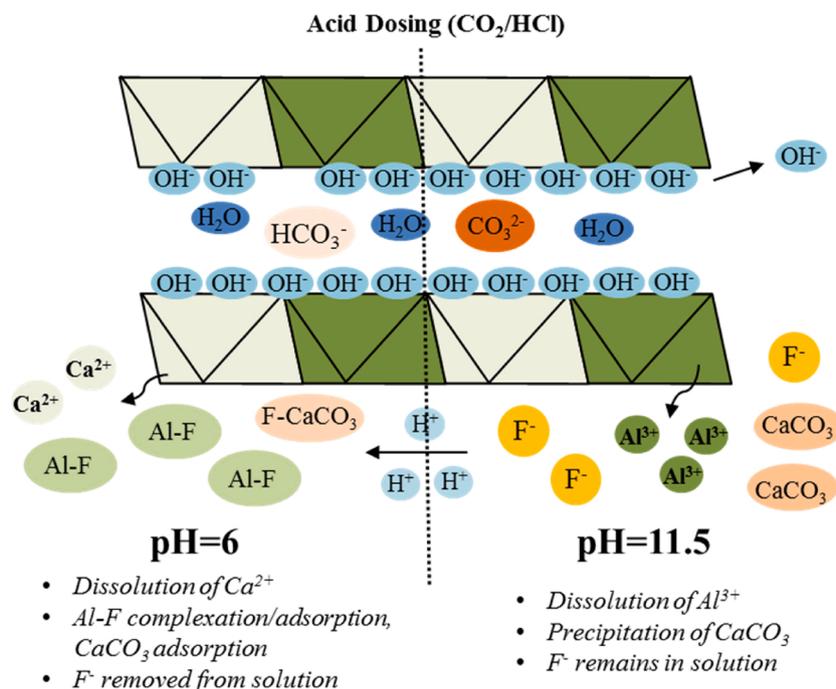
Fig. 7. Schematic drawing of proposed dissolution-complexation/adsorption mechanism.
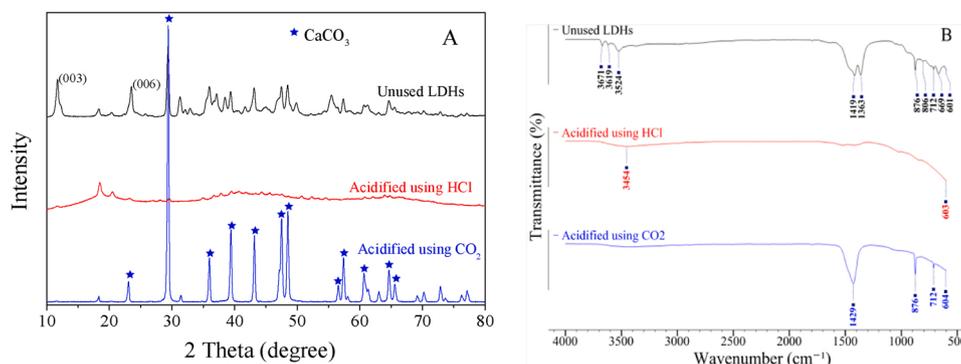

Fig. 8. XRD patterns (A) and FTIR spectra (B) of the Ca-Al−CO$_3$ LDHs before and after experiments.

while they are generally amorphous and show increased performance at lower pH (<7) [50–53]. The main mechanism of F- uptake by Mg-Al LDHs (Mg-Al-NO$_3$ and Mg-Al-Cl LDHs) has been previously proposed as the result of exchange between aqueous F- and NO$_3$- or Cl- anions positioned in the Mg-Al LDHs interlayer [13]. However, our proposed removal mechanism is F- adsorption or complexation onto/into Al-containing species and CaCO$_3$ (in the case of CO$_2$ acidification), which can be supported by the characterization results. These results suggest that the layered hydrotalcite-like structure was damaged, F- was present and Al(OH)$_3$ and CaCO$_3$ (in the case of CO$_2$ acidification) were formed after the experiments. Apart from the SEM-EDX, XRD and FTIR characterization, additional research is recommended, such as transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS), to further examine the F- removal mechanism.

4. Conclusions

In the present work the effects of pH-adjusting acids on F- removal from water by Ca-Al-CO$_3$ LDHs were reported. Acidification by conventional acids like HCl or CO$_2$ led to a substantially increased performance of Ca-Al-CO$_3$ LDHs for F- removal at environmentally relevant concentrations (e.g., 10 mg/L) with a relatively lower LDHs dose than

that found in most of the literature. The observed F- removal under LDHs acidification to pH 6 with HCl and CO$_2$ were 62 and 92% (HCl), and 38 and 90% (CO$_2$) at LDHs doses of 0.2 and 1 g/L, respectively. Addition of HCl and CO$_2$ to LDHs suspensions led to changes to the LDHs structure, demonstrated by SEM, EDX, XRD, and FTIR. Leaching experiments, supported by PHREEQC modelling, strongly suggest that the main mechanism of F- removal by Ca-Al-CO$_3$ LDHs was F- adsorption or complexation onto/into various rehydrated mixed metal oxides which re-precipitate upon partial LDHs dissolution when acidifying. The benefits of the lower costs (cf. cost estimate calculation in SI) and lower residual anion concentrations lead to the recommendation to apply CO$_2$ as the acidification method in combination with Ca-Al-CO$_3$ LDHs. The reusability and feasibility of Ca-Al-CO$_3$ LDHs in column and real groundwater should be examed in future studies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jwpe.2021.101957.

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