

Fluoride Removal from Groundwater by Mineral-based Materials at Environmentally-relevant Concentrations

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**Fluoride Removal from Groundwater by
Mineral-based Materials at
Environmentally-relevant Concentrations**

Liangfu WEI

Fluoride removal from groundwater by mineral-based materials at environmentally-relevant concentrations

Dissertation

For the purpose of obtaining the degree of doctor
at Delft University of Technology
by the authority of the Rector Magnificus, Prof.dr.ir. T.H.J.J. van der Hagen
chair of the Board for Doctorates
to be defended publicly on

Tuesday 2 November 2021 at 10:00 o'clock

by

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Summary

Excessive fluoride (F^-) in drinking water due to natural and anthropogenic activities is a serious health hazard affecting humans worldwide. The weathering of primary rocks and leaching of fluoride-containing minerals in soils, as well as industrial activities (e.g., steel, aluminium, glass, electroplating), can cause F^- rich groundwaters. Groundwater is the major and preferred source of drinking water, also in developing countries. While the presence of permissible F^- in drinking water is beneficial for health, excessive F^- ($>1.5\text{mg/L}$) intake causes dental or skeletal fluorosis, or even cancer. Unfortunately, around 200 million people from 28 nations around the world are under the fate of fluorosis, with India and China being the worst affected countries. Therefore, the removal of the excess F^- from groundwater prior to drinking is important in terms of protection of public health.

Current defluoridation techniques can be generally grouped into precipitation, coagulation, membrane processes, electrochemical processes, and adsorption/ion exchange. Although considerable advancement has been made in defluoridation research, a universal and sustainable solution to this ongoing crisis still appears intangible. By means of comparison to over 100 different materials, it can be concluded that mineral-based materials are among the most promising for F^- removal for drinking water production. Therefore, this thesis focused on investigating F^- removal from groundwater by layered double hydroxides (LDHs), geopolymers, softening pellets and struvite. Alike various clays and rocks, these materials are composed primarily of minerals, (naturally) crystallized and have a periodic structure. These materials were selected, apart for their affinity for F^- removal, because of their low cost and local availability, for example due to being waste or by-products from industrial operations.

Chapter 2 provides a comparative assessment of eight mineral-based materials with advantageous structural properties for F^- uptake: layered-double-hydroxides (LDHs), geopolymers, softening pellets and struvite. The strongest F^- affinity was observed for the Ca-based materials (Ca-Al- CO_3 LDHs, slag-based geopolymer, softening pellets). At higher initial F^- concentrations ($>20\text{ mg/L}$), the dominant removal mechanism is proposed to be precipitation of CaF_2 . At lower initial F^- concentrations ($<10\text{ mg/L}$), the main mechanism is considered to be F^- adsorption or anion exchange. Although the softening pellets had the highest Ca-content (96-97%; XRF), their dense structure and consequent low BET surface

area (2-3 m²/g), resulted in poorer performance than the Ca-based LDHs and slag-based geopolymer. Nevertheless, geopolymers, as well as struvite, are currently not considered of interest for application in water treatment, as they would need modification due to their poor stability or F⁻ leaching.

In chapter 3, F⁻ removal by Ca-Al-CO₃ LDHs was investigated at environmentally-relevant concentration ranges (2-12 mg/L) to below the WHO guideline, with an emphasis on effects of LDHs' modification, as well as effects of initial F⁻ concentration, adsorbent dose, pH, temperature and co-existing ions. Ca-Al-CO₃ 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 NO₃⁻ was not observed, whereas at higher HCO₃⁻ and SO₄²⁻ concentrations (>250 mg/L) a slight reduction in F⁻ removal was observed. This study indicates the potential of Ca-Al-CO₃ LDHs as a cost-effective F⁻ removal technology, particularly when locally sourced and in combination with low-cost pH correction.

Chapter 4 showed that simultaneous acidification by conventional acids, such as HCl and CO₂ substantially increased the performance of Ca-Al-CO₃ 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 (HNO₃, H₂SO₄, H₃PO₄), the use of HCl and CO₂ does not lead to the introduction of potentially harmful or undesired anions. The addition of HCl and CO₂ 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-CO₃ LDHs was F⁻ adsorption or complexation onto/into various rehydrated mixed metal oxides which re-precipitated upon partial LDHs dissolution when acidifying.

Chapter 5 investigated the combination of granular Ca-Al-CO₃ LDHs packed beds with CO₂-based post acidification and microfiltration. This combination of treatment steps allows for sequential dissolution and precipitation of LDH-sourced calcium (Ca²⁺) and aluminum (Al³⁺), removed subsequently by a microfiltration step. We found that F⁻ removal was effective with CO₂ post-acidification from 5 mg F⁻/L to below the WHO standard of 1.5 mg/L. F⁻ removal capacity was observed to be exceeding 30.46 mgF/gLDHs and 15.06 mgF/gLDHs,

for batch and column mode, respectively. The column study demonstrated a slow and stable LDHs dissolution of 0.23g LDH per L of feed, leading to continuous and efficient F^- removal. Solids characterization by XRD confirmed precipitation of dissolved granular LDHs as particulates ($CaCO_3$ and hydrated Al oxides).

Overall, it can be concluded that out of the investigated mineral-based materials, Ca-based materials (Ca-Al- CO_3 LDHs, slag-based geopolymer, softening pellets) showed the strongest affinity to remove F^- . Ca-Al- CO_3 LDHs showed affinity for F^- in the environmentally-relevant concentrations but the defluoridation by Ca-Al- CO_3 LDHs is highly pH sensitive. Therefore, the combination of granular Ca-Al- CO_3 LDHs packed beds with CO_2 -based post acidification and microfiltration was developed as novel integrated method for efficient F^- removal.

Samenvatting

Hoge concentraties fluoride (F^-) in drinkwater, als gevolg van natuurlijke en antropogene activiteiten, is wereldwijd een ernstig gevaar voor de gezondheid van mensen. Verwerking van gesteente, uitspoelen van fluoride-houdende mineralen in bodems en industriële activiteiten (bijv. staal, aluminium, glas, galvaniseren) kunnen hoge concentraties F^- in grondwater veroorzaken. Grondwater is de belangrijkste voorkeursbron van drinkwater, ook in ontwikkelingslanden. Hoewel een lage concentratie F^- in drinkwater gunstig is voor de gezondheid, veroorzaakt overmatige inname van F^- ($> 1,5 \text{ mg/L}$) tand- of skeletfluorose of zelfs kanker. Wereldwijd lijden ongeveer 200 miljoen mensen uit 28 landen aan de gevolgen van fluorose aan de gevolgen van de hoge F^- concentraties. India en China zijn de zwaarst getroffen landen. Het verwijderen van F^- uit het grondwater voorafgaand aan het drinken is daarom belangrijk voor de bescherming van de volksgezondheid.

De huidige verwijderingstechnieken voor F^- kunnen verdeeld worden in precipitatie, coagulatie, membraan, elektrochemische en adsorptie/ionenuitwisseling processen. Hoewel er aanzienlijke vooruitgang is geboekt in het onderzoek naar F^- verwijdering, lijkt een universele en duurzame oplossing voor deze aanhoudende crisis nog steeds niet beschikbaar. Bhatnagar et al., 2011 onderzocht F^- verwijdering door 100 verschillende materialen en concludeerde dat materialen opgebouwd uit mineralen het meest veelbelovend zijn. Dit proefschrift is daarom gericht op het onderzoeken van F^- -verwijdering uit grondwater door gelaagde dubbele hydroxiden (LDHs), geopolymeren, onthardingspellets en struviet. Net als verschillende kleien en gesteenten, zijn deze materialen voornamelijk samengesteld uit (natuurlijk) gekristalliseerde mineralen, en hebben ze een periodieke structuur. De onderzochte materialen zijn geselecteerd, afgezien van hun affiniteit voor F^- -verwijdering, vanwege hun lage kosten en lokale beschikbaarheid, bijvoorbeeld omdat het afval- of bijproducten zijn vanuit de industrie.

Hoofdstuk 2 bevat een vergelijking van acht materialen opgebouwd uit mineralen met gunstige structurele eigenschappen voor F^- opname: gelaagde dubbele hydroxiden (LDHs), geopolymeren, onthardingspellets en struviet. De sterkste F^- verwijdering werd waargenomen voor de materialen opgebouwd uit Ca mineralen (Ca-Al- CO_3 LDHs, op slakken gebaseerd geopolymeer, onthardingspellets). Bij hogere initiële F^- concentraties ($>20 \text{ mg/L}$), wordt het

neerslaan van CaF_2 als het dominante verwijderingsmechanisme beschouwd. Bij lagere initiële F^- concentraties ($<10 \text{ mg/L}$), was het belangrijkste mechanisme adsorptie van F^- of anionuitwisseling. Hoewel de onthardingspellets het hoogste Ca-gehalte hadden (96-97%; XRF), resulteerde hun dichte structuur en het daardoor lage BET-oppervlak ($2\text{-}3 \text{ m}^2/\text{g}$) in slechtere prestaties dan de op Ca gebaseerde LDHs en op slakken gebaseerd geopolymeer. Desalniettemin worden geopolymeren, evenals struviet, momenteel niet aanbevolen voor toepassing in waterzuivering, omdat er nog aanpassingen nodig zijn vanwege hun slechte stabiliteit of uitloging van F^- .

In hoofdstuk 3 werd F^- verwijdering door Ca-Al-CO_3 LDHs onderzocht voor een concentraties geobserveerd in het milieu ($2\text{-}12 \text{ mg/L}$), naar de WHO-richtlijn voor drinkwater. De studie onderzocht de effecten van LDHs modificatie, evenals effecten van F^- concentratie, adsorbent dosis, pH, temperatuur en concurrerende ionen. Ca-Al-CO_3 LDHs, onbehandeld, verkalkt of na microgolfbehandeling, vertoonden affiniteit voor F^- verwijdering uit synthetisch grondwater. Een F^- verwijdering was geobserveerd tussen de $6,7\text{-}8,4 \text{ mg F}^-/\text{g}$ LDHs bij grondwaterrelevante pH, met een hogere capaciteit bij een lagere pH (<8) en lagere temperatuur ($12 \text{ }^\circ\text{C}$, in vergelijking met $25 \text{ }^\circ\text{C}$ en $35 \text{ }^\circ\text{C}$). Aangezien verkalken en microgolfbehandeling slechts een marginale verhoging van F^- verwijdering opleverden, lijkt het gebruik van onbehandelde LDH's de praktisch meest haalbare optie. Voor de onbehandelde LDH's werd geen concurrentie met Cl^- en NO_3^- waargenomen, terwijl bij hogere HCO_3^- en SO_4^{2-} concentraties ($>250 \text{ mg/L}$) een lichte daling van F^- verwijdering werd waargenomen. Deze studie geeft het potentieel aan van Ca-Al-CO_3 LDHs als een kosteneffectieve F^- verwijderingstechnologie, vooral wanneer deze lokaal wordt geproduceerd en in combinatie met goedkope pH-correctie.

In Hoofdstuk 4 werd aangetoond dat aanzuring door conventionele zuren, zoals HCl en CO_2 , de prestatie van Ca-Al-CO_3 LDHs voor F^- verwijdering substantieel verbeterde, waarbij het gebruik van HCl en CO_2 in vergelijking met andere zuren (HNO_3 , H_2SO_4 , H_3PO_4) niet leidt tot de introductie van potentieel schadelijke of ongewenste anionen. F^- concentraties werden verlaagd tot onder de WHO-richtlijnwaarde (1.5 mg/L). De toevoeging van HCl en CO_2 aan LDHs-suspensies zorgde wel voor veranderingen in de LDHs-structuur. Uitlogingsexperimenten, ondersteund door PHREEQC-modellering en karakterisering (SEM-EDX, XRD en FTIR), suggereren sterk dat het belangrijkste mechanisme LDHs F^- adsorptie of complexering op/in verschillende gerehydrateerde gemengde metaaloxiden was, die opnieuw neersloeg bij het aanzuren.

In Hoofdstuk 5 wordt de combinatie van granulaire Ca-Al-CO₃ LDHs in een gepakte kolom met op CO₂ gebaseerde postverzuring en microfiltratie onderzocht. Deze combinatie van behandelingsstappen zorgt voor een opeenvolgende oplossing en precipitatie van calcium (Ca²⁺) en aluminium (Al³⁺) afkomstig uit LDH, die vervolgens worden verwijderd tijdens de microfiltratiestap. We ontdekten dat verwijdering van F⁻ effectiever was na aanzuring met CO₂: van 5 mg F⁻/L tot onder de WHO-norm van 1,5 mg/L. Een F⁻ verwijderingscapaciteit hoger dan 30,46 mgF/gLDHs en 15,06 mgF / gLDHs werd geobserveerd, respectievelijk voor batch- en kolommodus. De kolomstudie toonde een langzame en stabiele LDH-oplossing van 0,23 g LDH per liter aanvoer, wat leidde tot een continue en efficiënte F⁻ verwijdering. Karakterisering van vaste stoffen door XRD bevestigde het neerslaan van opgeloste granulaire LDHs (CaCO₃ en gehydrateerde Al-oxiden).

Over het algemeen kan worden geconcludeerd dat van de onderzochte materialen, de materialen op basis van Ca mineralen (Ca-Al-CO₃ LDHs, geopolymeer op basis van slakken, onthardingspellets) de grootste affiniteit vertoonden om F⁻ te verwijderen. Ca-Al-CO₃ LDHs vertoonden affiniteit voor F⁻ in de concentraties relevant in het milieu, maar de F⁻ verwijdering door Ca-Al-CO₃ LDHs is zeer pH-gevoelig. Daarom werd de combinatie van granulaire Ca-Al-CO₃ LDHs-gepakte kolom met op CO₂ gebaseerde postverzuring en microfiltratie ontwikkeld als een nieuwe geïntegreerde methode voor efficiënte F⁻ verwijdering.

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Liangfu Wei

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Chapter 1

Introduction and scope of the thesis

1 Fluoride in water

The element fluorine is the most electronegative and reactive of all chemical elements and thus rarely occurs naturally in the elemental state and is found as fluorides in the environment (Gupta and Ayoob, 2016). Fluorides account for about 0.06-0.09% of the earth's crust in total and are found at high levels in various minerals, including fluorite (CaF_2), phosphate rock, cryolite, apatite, mica, and hornblende (Murray, 1986). The electronegative nature of fluorine demonstrates that it is easy to obtain a negative charge in the solution to form fluoride ion (F^-) (Chambers and Holliday, 1975). The weathering of primary rocks and leaching of fluoride-containing minerals in soils, as well as industrial activities (e.g., steel, aluminium, glass, electroplating) appear to be the main contributing factors of F^- into water (Gupta and Ayoob, 2016).

Rivers and lakes generally contain less than 0.5 mg/L of F^- while seawater typically contains about 1 mg/L (Hem, 1985). In groundwater, however, high concentrations of F^- can occur, depending on the nature of the rocks and the occurrence of F^- -bearing minerals (Hem, 1985). Groundwater constitutes 97% of global freshwater and is used for drinking by more than 50% of the world population (Howard et al., 2006). It is the preferred source of drinking water in rural areas, particularly in developing countries as it is microbially safe (Meenakshi and Maheshwari, 2006). In India, it is estimated that 80% of domestic consumption in rural and 50% in urban areas are met by groundwater sources alone (Maria, 2003). The presence of F^- in drinking water, within permissible limits of 0.5-1.0 mg L^{-1} , is beneficial for the production and maintenance of healthy bones and teeth, while excessive intake of F^- causes dental or skeletal fluorosis which is a chronic disease manifested by mottling of teeth in mild cases, softening of bones and neurological damage in severe cases (Krupadam et al., 2010). Particularly in children, excess intake of fluoride leads to various diseases including osteoporosis, arthritis, and cancer (Wambu et al., 2012). The maximum acceptable F^- concentration in water intended for human consumption recommended by the World Health Organization is 1.5 mg L^{-1} (World Health Organization, 2004).

However, the entry of F^- into groundwater aquifers as a geological pollutant has become a global concern (Gupta and Ayoob, 2016). Many countries have regions where the groundwater contains more than 1.5 mg L^{-1} of F^- due to its natural presence in the earth's crust, or discharge by agricultural and industrial activities, such as steel, aluminium, glass, electroplating (Mahramanlioglu et al., 2002). Fluorosis due to excessive concentration of F^-

affects around 200 million people worldwide and has been reported in at least 28 countries from South Asia, Africa, the Middle East, North, Central and South America, and Europe (Fawell and John., 2006). India and China, the two most populous countries are the worst affected by fluorosis, with approximately 67 million and 41 million exposed people, respectively (Gupta and Ayoob, 2016). Therefore, the removal of the excess F^- from groundwater prior to drinking is important in terms of protection of public health.

2 Fluoride removal

Although considerable advancement has been made in defluoridation research, a universal and sustainable solution to this ongoing crisis still appears intangible. Based on the nature of the mechanisms involved, defluoridation techniques can be generally grouped into precipitation, coagulation, membrane processes, electrochemical processes, and adsorption/ion exchange. Precipitation techniques involve the deposition of F^- by the addition of a suitable reagent such as lime and calcium salts (Eggers et al., 1991). Precipitation is an effective F^- removal method, but it cannot bring F^- to the required concentration levels for drinking water production, which is due to the solubility constraints of CaF_2 (Turner et al., 2005). Coagulation is another technology applied for F^- removal, involving complexation, electronic attraction and physical adsorption of F^- through the use of appropriate reagents such as aluminum salts, iron salts, polyaluminum chloride and alum (He et al., 2016; Lu et al., 2000b). Although the coagulation method is generally effective in defluoridation, the performance of F^- removal is greatly affected by stirring conditions and settling time, accompanied by the introduction of other ions such as SO_4^{2-} , Cl^- and Al^{3+} , and the production of a large amount of F^- -containing sludge (Gong et al., 2012). Membrane processes including reverse osmosis, nanofiltration and electro dialysis have been noted to be effective for F^- removal, but they are relatively expensive to install and complex to operate, making them unsuitable for rural water supply in developing counties (Ayoob et al., 2008a; Maheshwari, 2006). In the reverse osmosis process, pressure is applied to force feed water through a semipermeable membrane thereby removing dissolved solutes (including F^-) through rejection by the membrane, based on particle size and electrical charges (Schneider and Middlebrooks, 1983). Nanofiltration involves the removal of uncharged organic species on nanoscale by size exclusion, and ion removal by charge effects (Bart and Carlo, 2003). In the electro dialysis process, the separation is accomplished by alternately placing cation- and anion-selective

membranes in a parallel fashion across the current path to form an electro dialysis cell (Adhikary et al., 1989). In recent years, electrochemical techniques such as electrocoagulation and electrosorption have attracted much attention but the high costs during both installation and maintenance are still a major constraint for implementation (Ayoob et al., 2008a). Electrocoagulation utilizes an electrolytic process to generate a coagulant in situ by oxidation of an appropriate anodic material, then the coagulant ions react with F^- , initiating normal coagulation (Ming et al., 1987). The electrosorption technique combines theory of electrochemistry with adsorption and separation technology to enhance the sorption capacity of conventional systems (Chen et al., 2019). The processes that the solute species at the interface may be removed or exchanged for other solutes without greatly affecting the properties of the solid surface are generally called adsorption. Sorption is a more noncommittal term that could include other processes (Hem, 1985). Ion exchange is a stoichiometric process where any counter ion leaving the ion exchanger surface is replaced by an equivalent number of moles of another counter ion to maintain electro-neutrality of the ion exchanger (Loganathan et al., 2013). In contrast to ion exchange, adsorption is a more general term for retention of solutes at surfaces and sometimes is applied to all such effects but ion exchange is considered to occur at specific sites (Hem, 1985).

Adsorption is the most widely used method for excess F^- removal from water because of its effectiveness, convenience, ease of operation, simplicity of design, and economic and environmental considerations (Ho et al., 2011). With reference to F^- , the adsorption mechanism suggested was normally ion exchange between counter ions at positive surface sites (Meenakshi and Viswanathan, 2007; Miretzky and Cirelli, 2011). In the adsorption process, F^- gets concentrated and confined on to a small adsorbent mass (Ayoob et al., 2008a). Adsorption was considered as one of the main processes involved in this thesis.

3 F^- adsorbents

Various conventional and non-conventional adsorbents have been assessed for the removal of F^- from water, however, these materials have a number of drawbacks such as low efficiency, expensive, unstable, not environmentally friendly, only effective at an extreme pH (Fan et al., 2003a) and can't be separated or be used in column/continuous operations. The most frequently encountered adsorbents can be divided into aluminium-based adsorbents,

calcium-based materials, other metal oxides/hydroxides/oxyhydroxides materials, natural or synthetic materials and their modified materials. Activated aluminium, aluminium salts, alumina balls and other aluminium based adsorbents are widely used for the removal of F^- from water (Ghorai and Pant, 2005; Tripathy and Raichur, 2008). Although activated alumina is a robust adsorbent for fluoride uptake, it is expensive and its performance is affected by pH and the presence of co-ions in water such as SO_4^{2-} , Cl^- , HCO_3^- and PO_4^{3-} (Tressaud, 2006). Careful attention to residual Al^{3+} is always needed while using aluminium-based adsorbents for defluoridation of water because aluminium is a neurotoxin (Ayoob et al., 2008a). F^- can be removed by calcium-based materials through a combination of surface adsorption and precipitation reactions (Turner et al., 2005). However, precipitation cannot bring F^- to the required WHO standard due to the solubility constraints of CaF_2 . Double or triple metal oxides have been widely tested as high defluoridation adsorbents, while they are generally amorphous and show increased performance at lower pH (<7) (Han et al., 2010; Wang et al., 2017; Wu et al., 2007; Yang et al., 2015). Rare earth oxide-based materials have shown high fluoride removal efficiency in batch mode but in some cases these materials have been found expensive and the optimum pH is in the acidic range (Bhatnagar et al., 2011). Some natural or synthetic materials such as zeolites and chitosan have limited F^- removal ability which can be enhanced by modification such as coating Al^{3+} and Fe^{2+} on the surface, but a certain amount of metal ions can be released into the water resulting in second-pollution (Onyango et al., 2006; Swain et al., 2009; Viswanathan and Meenakshi, 2008). Some types of waste materials (e.g. red mud, sludge) have been investigated as low-cost adsorbents, but the potential leaching of toxic metals from these wastes to treated water must continuously be monitored (Çengeloğlu et al., 2002; Sujana et al., 1998). Bone char has been successfully used in some installations for defluoridation of drinking water. One of the limitations of the bone char method is that its capacity reduces after successive regenerations, and hence very often the medium is discarded rather than regenerated (Kawasaki et al., 2009).

By means of comparison to over 100 different materials, it can be concluded that mineral-based materials are promising for F^- removal for drinking water production (Bhatnagar et al., 2011), due to the fact that mineral-based materials generally possess a layered or reticulate structure with electropositive multivalent metal ions (Miretzky and Cirelli, 2011). This positive charge on the surface could attract the small F^- anions (Nie et al., 2012). Mineral-based materials such as various clays and rocks are composed primarily of naturally crystallized periodic structures (Liittge and Arvidson, 2008). Because of their low

cost and local availability, natural materials such as clays, or certain waste or by-products from industrial operations such as softening pellets, struvite, slag and fly ash are classified as low-cost materials. They are inexpensive and consequently can be used in less developed countries, especially in rural areas.

4 Aim and scope of the study

This study aimed to investigate whether layered double hydroxides (e.g. Ca-Al-LDHs), geopolymers (slag-, fly ash-, metakaolin-based), softening pellets and struvite are suitable alternatives for F^- removal from groundwater to the WHO drinking water standard of 1.5 mg/L. The performance of the Ca-Al- CO_3 LDHs was further examined under different environmentally-relevant water compositions (including, initial F^- concentration, pH, temperature and co-existing ions). In addition, various pH-adjusting acids (HCl, HNO_3 , H_2SO_4 , H_3PO_4 , CO_2) were investigated to enhance F^- removal by Ca-Al- CO_3 LDHs. Also, the granulation of these Ca-Al- CO_3 LDHs was studied for application in packed beds with CO_2 -based post acidification. This section provides an overview of the investigated mineral-based and waste materials, including layered double hydroxides, geopolymers, softening pellets and struvite.

4.1 Layered double hydroxides (LDHs)

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, are a class of naturally occurring and synthetic anionic clays (Duan and Evans, 2006). The formula of LDHs can be generically represented by $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} [A^{m-}_{x/m} \cdot nH_2O]$, where M^{2+} is a divalent cation and M^{3+} represents a trivalent cation; A^{m-} is an interchangeable anion with charge m , x is a ratio between di- and trivalent cations, and n is the number of water molecules (Batistella et al., 2011b; Reichle, 1986). LDHs possess relatively large surface areas (20-120 m^2/g) and high anion-exchange capacities (3.0-4.8 meq/g) (Lv et al., 2007b). Due to the presence of large quantities of exchangeable anions and sizable interlayer spaces, LDHs and their modified products are effective adsorbents for removal of a variety of anionic and cationic pollution from contaminated waters (Wang et al., 2007).

LDHs and their modified products as adsorbents have been examined for use in removing P, NO_3^- , BrO_3^- , Cl^- , As(III) and heavy metals such as Cr(VI), Cu(II), Cd(II), Pb(II) from aqueous solutions (Batistella et al., 2011b; Caius, 2011; Caporale et al., 2013b; Das et al., 2006b; Halajnia et al., 2012b; Lazaridis et al., 2004b; Lv et al., 2009b; Pérez et al., 2006b).

Yu et al. (2012) synthesized 3D hierarchical flower-like Mg-Al-layered double hydroxides (Mg-Al-LDHs) via a solvothermal method. They indicated that the main adsorption mechanisms for As(V)/Cr(VI) removal by uncalcined and calcined LDHs were adsorption of anions onto their external surface and the structure reconstruction, respectively (Yu et al., 2012). Cheng et al. (2010) proposed that phosphate adsorption onto Zn-Al-LDHs (raw or calcined) attributed to a combination of different mechanisms, e.g., surface adsorption, ion exchange and ion incorporation during the LDHs rehydration (Cheng et al., 2010). Lv et al. (2009) prepared LDHs containing nitrate as the interlayer anion (NO_3 -LDHs) by a co-precipitation method and they indicated that NO_3 -LDHs exchange NO_3^- with chloride ions and transforms to Cl-LDHs for the removal process, and thus the chloride ion in solution can be retained by NO_3 -LDHs following an anion-exchange process (Lv et al., 2009b).

The maximum adsorption capacity of various LDHs for fluoride ions ranged from 1.84 to 319.8 mg/g (Batistella et al., 2011b; Chang et al., 2011a; Du et al., 2014b; Kameda et al., 2015a; Lv et al., 2007b; Mandal and Mayadevi, 2008b; Wang et al., 2007). Kameda et al. (2015b) proposed that F^- uptake by Mg-Al-LDHs (NO_3 ·Mg-Al LDHs and Cl·Mg-Al LDHs) is the result of exchange between aqueous F^- and NO_3^- or Cl^- anions intercalated in the Mg-Al LDHs interlayer (Kameda et al., 2015b). Lv et al. (2007) used calcined CO_3 ·Mg-Al LDHs (CLDHs) to remove fluoride and they proposed that the mechanism of defluoridation by CLDHs can be mainly explained as a reconstruction of CLDHs in a fluoride solution with the fluoride ions intercalated to LDHs (Lv, 2007b).

4.2 Geopolymers

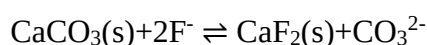
Geopolymers are alkali activated aluminosilicates, consisting of a solid reactive component that contains SiO_2 and Al_2O_3 , for example, active clays, fly ashes, pozzolanas and slag (López et al., 2014). The term “geopolymer” was first used by J. Davidovits in the late 1970s (Davidovits, 1991). The empirical formula can be represented as $\text{M}_n [-(\text{SiO}_2)_z-\text{AlO}_2]_n \cdot w\text{H}_2\text{O}$. Where M is the alkaline element or cation such as potassium, sodium or calcium; n is the degree of polycondensation or polymerization; z is 1,2,3 (Davidovits, 1991). The geopolymerization process involves a substantially fast chemical reaction under alkaline condition on Si-Al minerals that result in a three dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds (Bakri et al., 2011).

Geopolymers have been utilized for immobilizing and stabilizing pure or contaminated (mixed waste) forms of low-level radioactive waste and heavy metals as well (Dan et al.,

2005; Van Jaarsveld et al., 1999). In recent years, geopolymers have also been used as adsorbents for the removal of heavy metals and dye from aqueous solution (Chen et al., 2013; Cheng et al., 2012; Li et al., 2006; López et al., 2014). Al-Zhoon et al. (2011) synthesized highly amorphous geopolymer from waste coal fly ash to remove Pb(II) from aqueous wastewater and they reported that the synthesized geopolymer has higher removal capacity for lead ions when compared with that of raw coal fly ash (Al-Zboon et al., 2011b). Li et al. (2006) proposed that the fly ash derived geopolymeric adsorbents show higher adsorption capacity for crystal violet than methylene blue and the synthesised materials exhibit much higher adsorption capacity than fly ash itself and natural zeolite (Li et al., 2006). Alshaaer et al. (2015) reported that the maximum adsorption efficiency of zeolitic tuff-metakaolin (ZM) geopolymers is 7.8 mg Cu²⁺/g of adsorbent which indicates that ZM-geopolymers can be used in environmental applications including the clean-up of industrial effluents and wastewaters (Alshaaer et al., 2015).

4.3 Softening pellets

Softening pellets are a by-product of hardness removal in drinking water production (Graveland et al., 1983), a process where a base (e.g., lime) is dosed prior to a reactor with seeding material. On this seeding material, e.g., garnet or calcite (Rankin and Sutcliffe, 1999), a coating of CaCO₃ grows over time, called pellets. Periodically, the largest pellets are removed from the reactor, which are potentially an interesting waste product for F⁻ removal. The process that utilizes the reaction of F⁻-bearing wastewaters with calcite particles has been proposed since the 1970's (Augustyn et al., 1978; Simonsson, 1979). The chemical reaction is usually expressed as follows:



Yang et al. (1999) constructed a fixed bed reactor filled with calcite particles (mean strokes diameter, 0.20 mm) to treat synthetic wastewater containing HF, NaF, NH₄F or Na₂SiF₆ under various conditions (Yang et al., 1999a).

4.4 Struvite

Struvite is a crystalline substance composed of magnesium ammonium phosphate (MgNH₄PO₄·6H₂O), first identified in the 18th century (Griffith, 1978). Struvite occurs naturally in geochemical and biological systems and is commonly found as a precipitate during wastewater treatment (Abdelrazig and Sharp, 1988; De-Bashan and Bashan, 2004).

Struvite recovered from wastewater has been proposed as a new low-cost high quality fertilizer (De-Bashan and Bashan, 2004). Apart from being used to recycle N and P from wastewater, struvite has also been observed to remove arsenic (As) by adsorption (Rouff et al., 2015) and coprecipitation into the mineral structure (Ma and Rouff, 2012). As a low-cost mineral-based material, struvite is expected to be capable of F^- removal considering the affinity of Mg^{2+} for F^- (Ranjan et al., 2015).

5 Outline of the thesis

Thesis outline	Research questions
In Chapter 2 a comparative assessment was performed of eight mineral-based materials with advantageous structural properties for F^- uptake: layered-double-hydroxides, geopolymers, softening pellets and struvite.	i. What material shows the strongest affinity for F^-? ii. What is the main mechanism of F^- removal by these materials?
Chapter 3 presents the results of F^- removal by Ca-Al- CO_3 LDHs at environmentally-relevant concentration ranges 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.	i. What is the affinity of Ca-Al-CO_3 LDHs to F^- at 2-12 mg/L? ii. What factors impact F^- removal and what is the proposed mechanism for F^- removal? iii. What is the effect of modification on the surface properties of LDHs?

Chapter 4 presents the results of various pH-adjusting acids (HCl, HNO₃, H₂SO₄, H₃PO₄, CO₂) on F⁻ removal by Ca-Al-CO₃ LDHs from water at environmentally relevant F⁻ concentrations.	i. What is the impact of various pH-adjusting acids on F⁻ removal by Ca-Al-CO₃ LDHs? ii. What is the effect of acids on the LDHs and water composition? iii. What is the proposed main mechanism for F⁻ removal?
Chapter 5 presents the results on the combination of granular Ca-Al-CO₃ LDHs packed beds with CO₂-based post acidification and microfiltration in F⁻ removal.	i. What is the optimal method for the granulation of Ca-Al-CO₃ LDHs? ii. How to use a granular Ca-Al-CO₃ LDHs packed bed to remove F⁻?
Chapter 6 represents an overall discussion and gives the overall results. Implications for the drinking water practice are described, and recommendations are given for future research and practical applications.	

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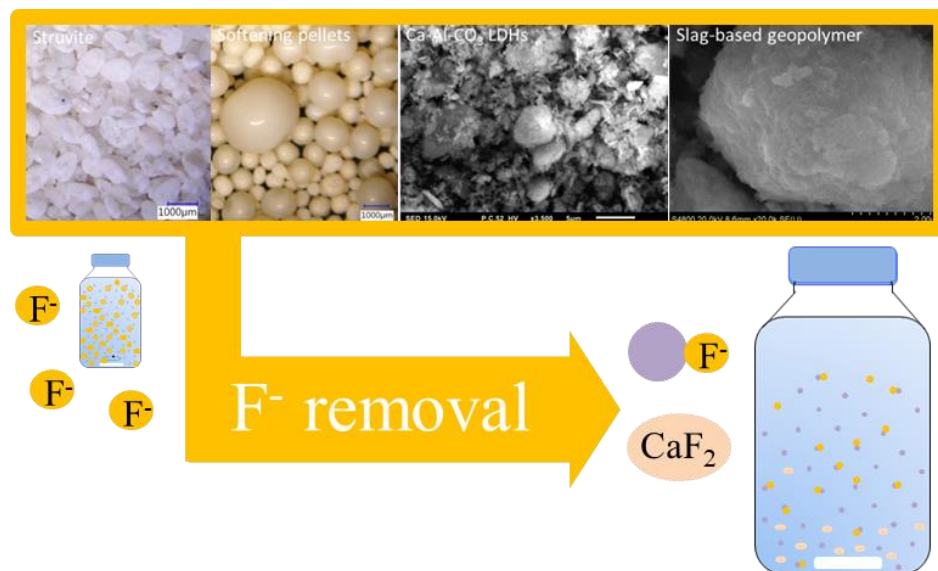
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Chapter 2

Comparative study of low-cost fluoride removal by softening pellets geopolymers layered double hydroxides and struvite



This Chapter is based on:

Wei L., Li Z., Ye G., Rietveld L.C., van Halem D. (2021), Comparative study of low-cost fluoride removal by layered double hydroxides, geopolymers, softening pellets and struvite, *Environmental Technology*, 1:20.

Abstract:

Excessive F^- in drinking water due to natural and anthropogenic activities is a serious health hazard affecting humans worldwide. In this study, a comparative assessment was made of eight mineral-based materials with advantageous structural properties for F^- uptake: layered-double-hydroxides (LDHs), geopolymers, softening pellets and struvite. These materials are considered low-cost, for being either a waste or by-product, or can be locally-sourced. It can be concluded that Ca-based materials showed the strongest affinity for F^- (Ca-Al- CO_3 LDHs, slag-based geopolymer, softening pellets). The main mechanism of F^- uptake on Ca-Al- CO_3 LDHs, Mg-Al-Cl LDHs, slag-based geopolymers and softening pellets was found to be sorption at low initial F^- concentrations (<10 mg/L) whereas precipitation as CaF_2 is proposed to play a major role at higher initial F^- concentrations (>20 mg/L). Although the softening pellets had the highest Ca-content (96-97%; XRF), their dense structure and consequent low BET surface area ($2-3$ m²/g), resulted in poorer performance than the Ca-based LDHs and slag-based geopolymers. Nevertheless, geopolymers, as well as struvite, were not considered to be of interest for application in water treatment, as they would need modification due to their poor stability and/or F^- leaching.

1. Introduction

Excessive F^- intake via drinking water, at concentrations above 1.5 mg/L, causes dental or skeletal fluorosis (Krupadam et al., 2010). Fluorosis due to F^- in drinking water has affected around 200 million people from 35 nations over the world (Ayoob and Gupta, 2006). In order to mitigate F^- exposure through drinking water, various methods have been developed to remove F^- from water. Particularly, F^- sorption and precipitation are methods of interest, as F^- ions are small and, as such, difficult to remove with most separation technologies, including membranes (Craig et al., 2015). In the past several decades, over 100 materials have been developed for the removal of F^- (Bhatnagar et al., 2011), including, activated alumina and rare earth oxide-based materials (Bahena et al., 2002; Jagtap et al., 2011). Particularly mineral-based materials are promising for F^- removal for drinking water production (Bhatnagar et al., 2011), due to the fact that mineral-based materials generally possess a layered or reticulate structure with electropositive multivalent metal ions (Miretzky and Cirelli, 2011). This positive charge on the surface could attract the small F^- anions (Nie et al., 2012).

Table 1 provides an overview of tested mineral-based materials, illustrating the variability in performance for F^- removal capacity (q_e). The materials with high q_e , such as Mg-Al- CO_3 LDHs and calcium-rich Attapulgite, have generally been tested at F^- concentrations higher than typically found in natural groundwater, complicating extrapolation to field-relevant conditions. An additional challenge is that most well-performing materials, such as nano goethite (Mohapatra et al., 2010) and CaO nanoparticles (Patel et al., 2009), are not widely available, making their supply chain for rural water supply challenging. Finally, quick lime and limestone could not obtain an equilibrium F^- concentration below 7.9 mg/L, due to the solubility constraints of CaF_2 , making it unacceptable for drinking water production (Turner et al., 2005).

Various mineral-based materials have thus been tested to remove F^- from water, but affordable and accessible materials for typical F^- concentrations in natural groundwater remain limited. The objective of this study is, therefore, to perform a comparative assessment of low-cost mineral-based materials, from the perspective of their F^- removal capacity, structure and stability. Eight different materials were selected, based on their presumed affinity for F^- , as their structure/composition resembles earlier reported F^- materials: Layered Double Hydroxides (LDHs) (Ca-Al- CO_3 LDHs and Mg-Al-Cl LDHs), geopolymers (slag-, fly

ash-, metakaolin-based), softening pellets (two types) and struvite. The first being a natural clay and the others being sourced from waste streams, namely, from industrial processes, drinking water treatment and wastewater treatment.

Table 1. Overview of F⁻ removal by mineral-based materials

Materials	q _e max (mg/g)	Experimental conditions				References
		F range (mg/L)	Dosage (g/L)	pH	Temperature	
Quartz	0.19	2.5×10 ⁻⁵	16.7	6	-	(Fan et al., 2003b)
Calcite	0.39	-6.34×10 ⁻²	16.7	6	-	(Fan et al., 2003b)
Kaolinite	0.667	5	1-8	6-7	32±2°C	(Srimurali et al., 1998)
Laterite	0.8461	10-50	1	7.5	30°C	(Sarkar et al., 2006)
Bentonite	1.15	5	1-8	6-7	32±2°C	(Srimurali et al., 1998)
Magnesia-loaded fly ash	11.61	5-20	2.5	4	30°C	(Geethamani et al., 2013)
Hydroxyapatite	16.38	5-50	0.5	7	25	(Nie et al., 2012)
Quick lime	16.67	10-50	1-10	-	25±2°C	(Islam and Patel, 2007)
Lime stone	43.1	0-100	1	8	298K	(Jain and Jayaram, 2009)
Nano-goethite	59	10-150	1	5.75	303K	(Mohapatra et al., 2010)
Attapulgit (calcium-rich)	140.1	10-600	20	8	25	(Yin et al., 2015)
CaO Nanoparticles	163.3	10-100	0.6	2-8	25±1°C	(Patel et al., 2009)
Mg-Al-CO ₃ LDHs	319	5-2500	3	6	30±1°C	(Lv et al., 2007b)

LDHs and their modified products are considered as effective adsorbents for removal of a variety of anionic and cationic pollutants from aqueous solutions such as F⁻, Cl⁻, BrO₃⁻, P, NO₃⁻, As(III) and heavy metals such as Cr(VI), Cu(II), Cd(II), Pb(II) (Batistella et al., 2011b; Caius, 2011; Caporale et al., 2013b; Das et al., 2006b; Halajnia et al., 2012b; Lazaridis et al., 2004b; Lv et al., 2009b; Pérez et al., 2006b). Slag, fly ash and metakaolin are solid precursors of geopolymers and also have promising removal capacities for F⁻ (Geethamani et al., 2013;

Horváth et al., 2003; Islam and Patel, 2011). However, F^- removal by geopolymers is rarely reported. Softening pellets are spherical crystal beads of calcite nature and a waste product of hardness removal in pellet crystallization reactors (Rankin and Sutcliffe, 1999). Other calcium carbonate rich materials such as calcite particles, limestone and eggshell have been observed to have affinity for F^- sorption (Bhaumik et al., 2015; Simonsson, 1979; Yang et al., 1999b), making softening pellets an attractive alternative material. Struvite is magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$, MAP) (Brunet et al., 2007) and occurs naturally in geochemical and biological systems (Abdelrazig and Sharp, 1988; De-Bashan and Bashan, 2004). Struvite recovered from wastewater has been observed to remove arsenic (As) through adsorption (Rouff et al., 2015) and co-precipitation (Ma and Rouff, 2012), but has so far not been investigated for F^- removal.

2. Materials and methods

2.1 Materials and their preparation

Ca-Al- CO_3 LDHs and Mg-Al-Cl LDHs were supplied by Nabaltec (Germany) and Shaoyang Tiantang Additives Chemical Co., Ltd (China), respectively. Three types of geopolymers, slag-, fly ash- and metakaolin-based geopolymers, were prepared in the laboratory using commercial blast furnace slag (ORCEM, the Netherlands), fly ash (VLIEGASUNIE BV, the Netherlands), and metakaolin (Sigma-Aldrich). The softening pellets and struvite were obtained from full-scale installations, Dutch groundwater treatment plants (Bunnik and Sint Jansklooster) and a crystallization reactor, respectively.

The preparation process of geopolymers was as follows: 100g of solid precursors was mixed with 14M NaOH solution using a molar ratio of $SiO_2/Na_2O=1.0$. Geopolymer paste then started to form, which was mixed for 3-5min to give complete homogenization. Then the mixtures were put in a polypropylene bottle (200mL) precured for 28 days in a curing chamber, which had a temperature of 20 °C (Al-Zboon et al., 2011a). Before use, apart from the LDHs, all materials were crushed using a ball mill, then washed using deionized water at least three times and dried in an oven at 65 °C for 24h (25 °C for struvite).

F^- solutions with different concentrations were prepared with sodium fluoride (NaF) (Sigma-Aldrich) as the source. 2.21g NaF was dissolved in 1L deionized water to prepare the stock solution and then diluted into desired concentrations.

2.2 Characterization of materials

Digital images of the materials were taken by a digital microscope (KEYENCE VHX-5000). The specific surface area of the materials was determined by a gravimetric nitrogen Brunauer-Emmett-Teller (BET) specific surface area analysis device (Micrometrics Gemini VII 2390 V1.03). The chemical composition was determined by X-ray fluorescence (Panalytical Epsilon 3 XL). The surface morphology was carried out using the scanning electron microscope (SEM) (JEOL JSM-IT100).

2.3 Batch experiments

Batch equilibrium experiments were conducted in six glass bottles (100 mL with cap) with 100 mL F^- solutions at room temperature ($25 \pm 1^\circ C$). Initial solutions were adjusted to pH 8.5 (after materials dosing) using HCl (0.1 M) and NaOH (0.1 M), because F^- -containing groundwater, e.g. in China, tend to have a $pH > 8$ (Wen et al., 2013). The initial F^- concentrations were 2, 5, 10, 20, 40 and 80 mg/L. For the softening pellets, struvite and geopolymers, the dose was 20 g/L. For the Ca-Al- CO_3 LDHs and Mg-Al-Cl LDHs, the dose was 1 g/L and 10g/L, respectively, which was adjusted according to their performance in preliminary experiments. The results of preliminary experiments indicated that the equilibrium time for LDHs, geopolymers, softening pellets and struvite were 1 day, 7 days, 7 days and 4 days, respectively. After constant stirring for equilibrium, the solutions were filtered through a $0.45 \mu m$ membrane and were then analyzed by Ion chromatography (IC) (Metrohm, Switzerland).

The equilibrium uptake capacity (q_e : mg/g) of the materials at different initial F^- concentrations were calculated using the formula:

$$q_e = \frac{(C_0 - C_e)V}{m},$$

where C_0 (mg/L) and C_e (mg/L) are initial and equilibrium F^- concentrations, respectively; V (L) is the initial volume of solution; and m (g) is the mass of the material.

2.4 Ion leaching from materials

Ion leaching experiments were carried out by adding the materials (the same dose as the batch equilibrium experiments) into 100 mL of deionized water, which had been adjusted to pH 8.5 by dosing HCl (0.01M) and NaOH (0.01 M). Then the mixture was to stand for the same amount of time as the batch equilibrium experiments, and was then filtered by $0.45 \mu m$

membrane. The concentrations of cations (K^+ , Ca^{2+} , Na^+ , Mg^{2+} , NH_4^+) and anions (F^- , Cl^- , NO_3^- , NO_2^- , PO_4^{3-} , SO_4^{2-}) leaching from materials were measured using IC.

2.5 Dissolution and precipitation modeling using PHREEQC

PHREEQC is a geochemical model that can be used in speciation and saturation-index calculations, batch-reaction, one-dimensional reactive-transport, and inverse modeling (Parkhurst and Appelo, 2013b). In this study, PHREEQC was employed to calculate the dissolution of materials (softening pellets and struvite) and precipitation of calcium fluoride (CaF_2) and to calculate the solubility and relative thermodynamic stability of the materials. To study dissolution, a beaker was defined in the model with demineralized water to which the minerals calcite and (or) struvite were added. Step-wise, the minerals dissolved to equilibrium, and the concentrations and saturation indexes were calculated and plotted. The thermodynamic information on struvite was added because the phreeqc.dat database did not contain this information (included in supplementary data). For precipitation, F^- solution was defined by using the experimental major-ion data. Detailed descriptions of simulation and input files can be found in example 2 and 3 from Parkhurst and Appelo (Parkhurst and Appelo, 2013b).

3. Results and discussion

3.1 Digital microscope and SEM images

Figure 1 shows the digital microscope and SEM images of LDHs (A), geopolymers (B), softening pellets (C) and struvite (D). The SEM images of LDHs show that Ca-Al- CO_3 LDHs (1-5 μm) has finer particles than Mg-Al-Cl LDHs (5-40 μm). The particle sizes of geopolymers were distributed from approximately 1 to 100 μm . A flake structure was observed for the metakaolin-based geopolymer. Figure 1C depicts digital microscope and SEM images of the softening pellets, showing the dense structure of the crystal. The softening pellets ranged in size from 0.5 mm to approximately 2 mm. Figure 1D depicts images by digital microscope and SEM of the struvite, and illustrates that the crystal is constructed from small subunits with porous nature. The struvite particles were approximately 1 mm. The particle sizes of the crashed softening pellets and struvite were in the range from 1-5 μm .

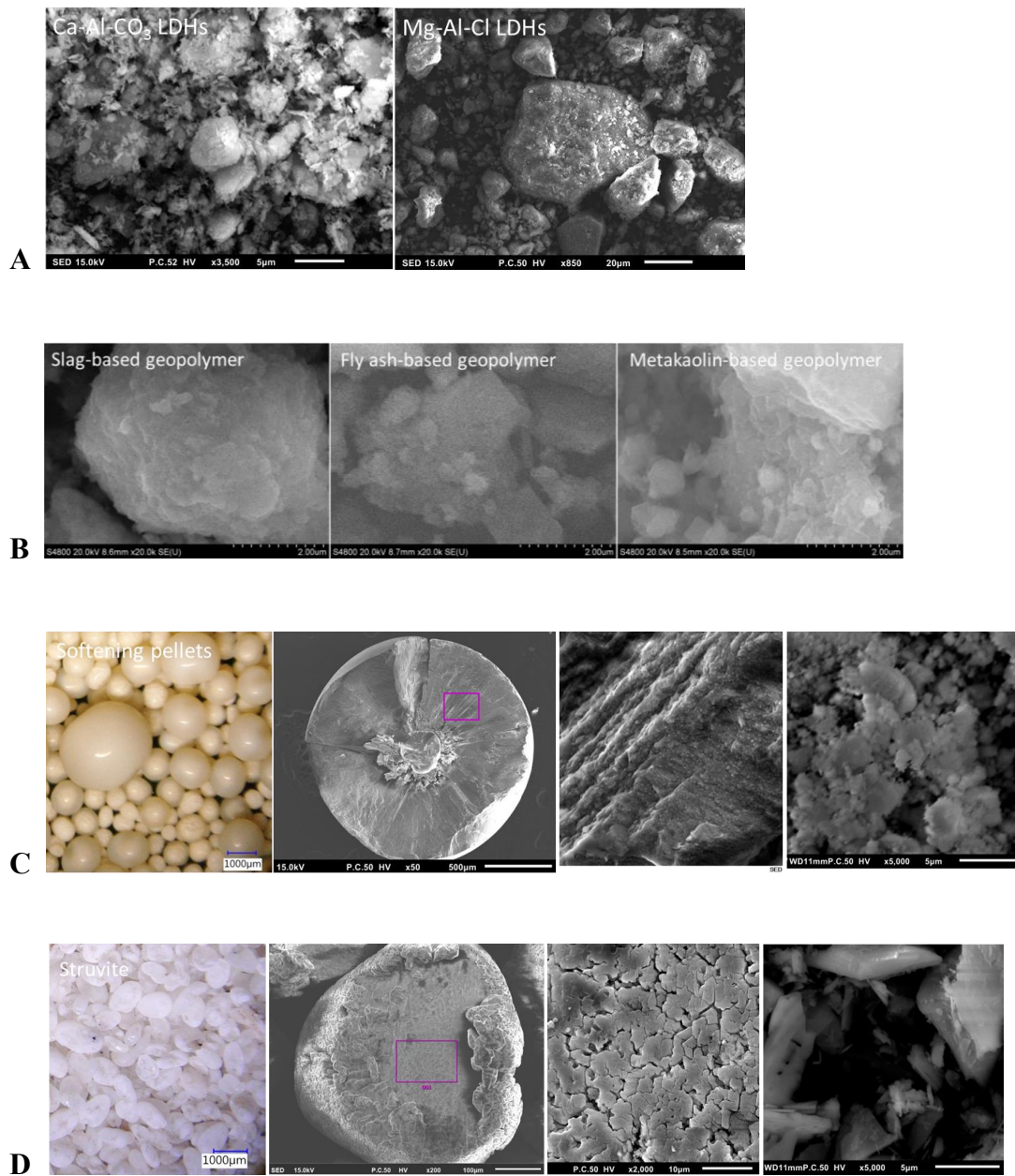


Figure 1. Digital microscope and SEM images of LDHs (A), geopolymers (B), softening pellets (C) and struvite (D).

3.2 Specific surface area (BET) and chemical composition (XRF)

It has been hypothesized that a high specific surface area is advantageous for sorbents, since it increases the number of surface sorption sites per unit area (Craig et al., 2015). However, it has also been suggested that the fractures, pore structure, size, and shape can impact the sorption rate and capacity by hindering the solute transport process (Craig et al., 2015; Hay et al., 2011). BET surface areas of the selected materials are presented in Table 2.

The results indicate that all materials have a relatively small specific surface area, below 10 m²/g, except for struvite (13.2 m²/g). Softening pellets had the lowest surface area (2.4 and 3.4 m²/g), which is lower than the value of 9.15 m²/g of commercial calcite (Gunawan et al., 2010). The surface areas of LDHs (7.6 and 8.4 m²/g) were relatively high, but still low compared with the values reported in literature (20-120 m²/g) (Lv et al., 2007b).

The chemical composition of the materials, from XRF analyses, indicates that CaO was the predominant component of the softening pellets and Ca-Al-CO₃ LDHs. Geopolymers consisted mainly of SiO₂ and Al₂O₃, although the slag-based geopolymer also contained a high CaO concentration. MgO was the predominant component of the Mg-Al-Cl LDHs and struvite.

Table 2. BET surface area and XRF analysis of chemical composition

Materials	BET surface area (m ² /g)	Chemical composition (XRF; wt%)		
Ca-Al-CO ₃ LDHs	7.6	CaO(71.4%)	Al ₂ O ₃ (28.5%)	
Mg-Al-Cl LDHs	8.4	MgO(52.7%)	Cl(24.1%)	Al ₂ O ₃ (17.5%)
Slag-based geopolymer	4.8	CaO(45.0%)	SiO ₂ (30.3%)	Al ₂ O ₃ (10.9%)
Fly ash-based geopolymer	2.7	SiO ₂ (54.1%)	Al ₂ O ₃ (24.0%)	Fe ₂ O ₃ (7.7%)
Metakaolin-based geopolymer	8.1	SiO ₂ (55.5%)	Al ₂ O ₃ (32.6%)	Na ₂ O(6.8%)
Softening pellets from Bunnik	3.4	CaO(99.3%)	Fe ₂ O ₃ (0.2%)	SO ₃ (0.1%)
Softening pellets from Sint Jansklooster	2.4	CaO(96.5%)	Fe ₂ O ₃ (2.5%)	SiO ₂ (0.5%)
Struvite	13.2	MgO(49.7%)	P ₂ O ₅ (49.1%)	Fe ₂ O ₃ (0.8%)

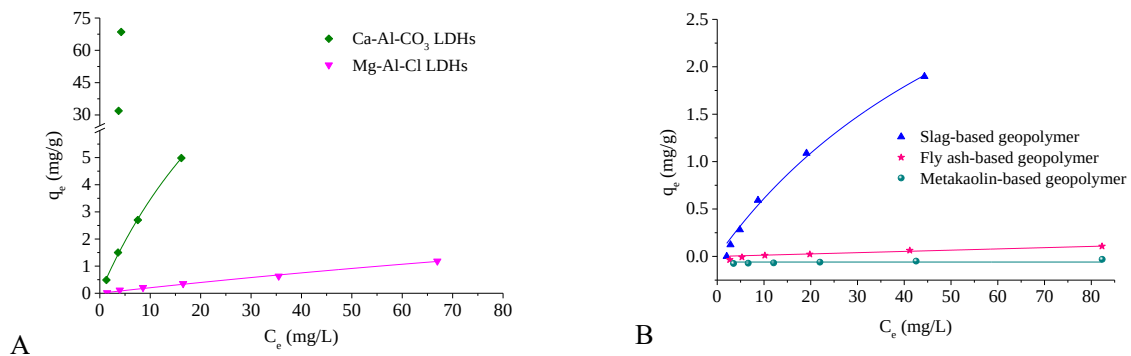
3.3 Fluoride uptake

Figure 2A shows that for the same initial F⁻ concentration, the F⁻ uptake by Ca-Al-CO₃ LDHs was higher than by Mg-Al-Cl LDHs. This cannot be explained by ion exchange, since it was reported that LDHs have greater affinity for multivalent inorganic anions compared with monovalent inorganic anions (Huang et al., 2015), although Kameda et al. (2015) proposed that F⁻ uptake by Mg-Al LDHs (Mg-Al-NO₃ and Mg-Al-Cl LDHs) is the result of exchange between aqueous F⁻ and NO₃⁻ or Cl⁻ anions positioned in the Mg-Al LDHs interlayer (Kameda et al., 2015b). However, adsorption is more likely, also because Ca²⁺ presents a stronger affinity for F⁻ than Mg²⁺ (Mohapatra et al., 2009). Alternatively, the sudden shift in F⁻ uptake at initial F⁻ concentrations over 40 mg/L by Ca-Al-CO₃ LDHs might also be explained by the precipitation of CaF₂.

In Figure 2B the F^- uptake by the geopolymers is presented. The results indicate that the slag-based geopolymer was effective in F^- removal, whereas the metakaolin-based geopolymer did not show a defluorination effect. The fly ash-based geopolymer only showed a limited F^- removal at high initial F^- concentrations (>20 mg/L), which may be explained by the release of F^- into the solution (Figure 4). The relatively good performance of slag-based geopolymers compared to fly ash- and metakaolin-based geopolymers may be explained by the presence of Ca^{2+} (Table 2).

Figure 2C shows the F^- uptake by softening pellets from softening reactors at water treatment plants Bunnik and Sint Jansklooster. It can be found that both pellets have a moderate affinity for F^- in relation to the small surface area. For the same initial F^- concentration, the F^- uptake by softening pellets from Bunnik was higher than that from Sint Jansklooster. This could be caused by a different pellet composition, i.e. softening pellets from Bunnik have a higher content of CaO, whereas Sint Jansklooster have a higher content of Fe_2O_3 (Table 2). It has been suggested that the F^- sorption capacity of Ca-rich attapulgite can go up to 140 mg/g, which was comparable with the sorption capacities of some nanoengineered materials (Yin et al., 2015). Such efficiencies were not achieved by softening pellets, likely due to the relatively low specific surface area.

The F^- uptake by struvite was tested at pH 7.5 and 8.5, and it was found to be highest at pH 7.5 (Figure 2D). The mechanism of F^- sorption onto struvite has not been studied previously, but earlier research on As adsorption indicated that As forms monodentate mononuclear surface complexes with struvite through the formation of a Mg-O-As bond as the main removal mechanism (Rouff et al., 2015). In addition, Brunet et al. (2007) found that tetracycline was removed via sorption and precipitation with struvite (approximately 16%-22%). Therefore, it is hypothesized that the uptake of F^- on struvite can also be explained by the formation of (surface) complexes.



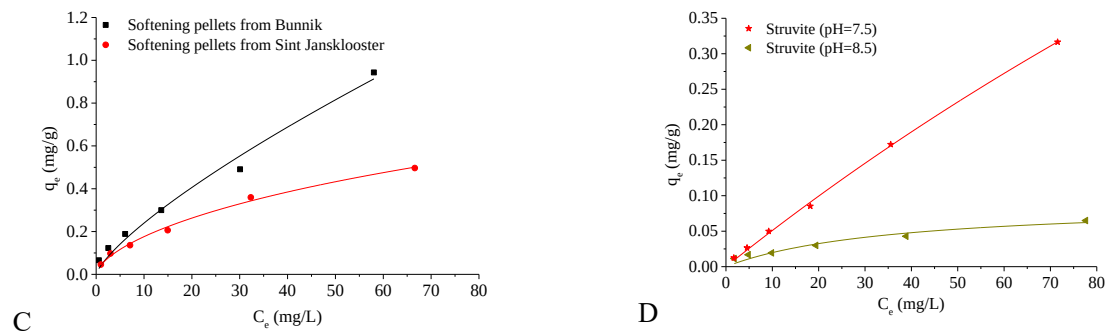


Figure 2. F^- uptake by LDHs (A), geopolymers (B), softening pellets (C) and struvite (D).

3.4 Equilibrium isotherms

Table 3 provides an overview of the Langmuir and Freundlich isotherm parameters for the studied materials. The F^- removal results obtained at higher F^- concentrations (>20 mg/L) for Ca-Al- CO_3 LDHs were considered to be influenced by the precipitation of CaF_2 and therefore excluded from this analysis. In addition, the fly ash- and metakaolin-based geopolymers did not show affinity for F^- sorption and were therefore not included in the isotherm model calculations. The Freundlich model provides a consistently better fit of the results than Langmuir. When viewing the Freundlich isotherm plots depicted in Figure 3, the values of the Freundlich exponent $1/n$ (except for Mg-Al-Cl LDHs) are smaller than 1 ($n > 1$) which is quite normal for sorption processes, still implying favorable conditions for higher initial concentrations and reflecting a chemisorption process (Foo and Hameed, 2010; Sousa et al., 2018; Yu et al., 2003).

Table 3. Isotherm parameters for F^- uptake on mineral-based materials.

Materials	Langmuir isotherm			Freundlich isotherm		
	$q_e = (q_m K_L C_e) / (1 + K_L C_e)$			$q_e = K_F C_e^{1/n}$		
	q_m (mg/g)	K_L (L/mg)	R_1^2	K_f (mg/g)(L/mg) $^{1/n}$	n	R_2^2
Ca-Al- CO_3 LDHs	20.83	0.0197	0.8	0.412	1.09	0.992
Mg-Al-Cl LDHs	3.02	0.0087	0.755	0.187	0.98	0.958
Slag-based geopolymer	5.23	0.0132	0.861	0.056	1.03	0.967
Softening pellets from Bunnik	1.20	0.0363	0.723	0.078	1.78	0.977
Softening pellets from Sint Jansloooster	0.63	0.0476	0.934	0.048	1.79	0.994
Struvite	0.08	0.0438	0.905	0.008	2.18	0.977

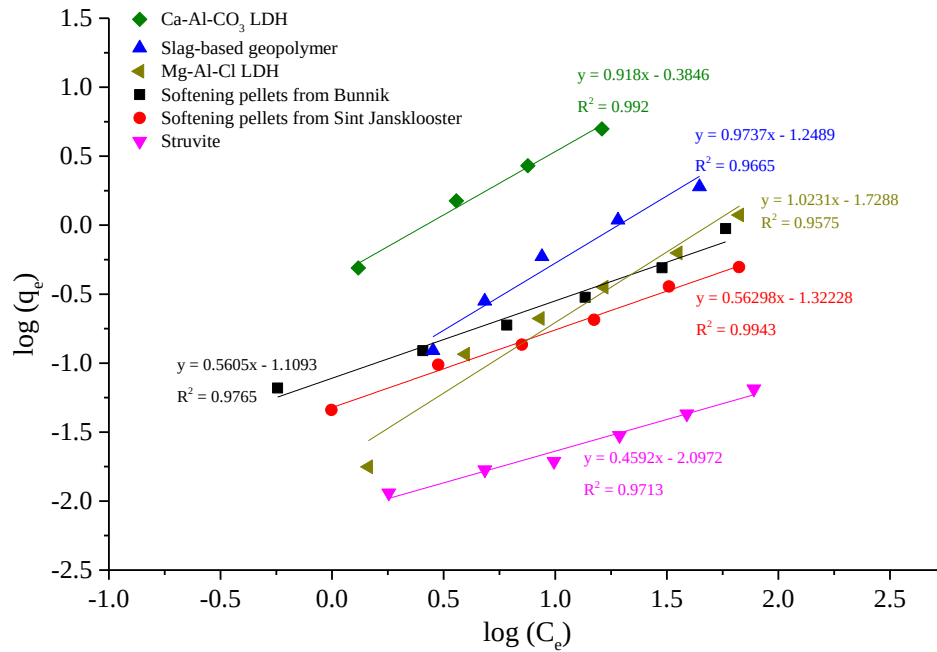


Figure 3. Freundlich isotherm plots of F^- uptake on mineral-based materials.

3.5 Ions leaching and PHREEQC calculation

The results of ion leaching are shown in Figure 4. It can be found that the concentrations of most ions leaching from softening pellets, Ca-Al- CO_3 LDHs, Mg-Al-Cl LDHs and the metakaolin-based geopolymer, remained below 10 mg/L. For Ca^{2+} , however, the concentrations were higher, with 13.2, 30.7 and 13.7 mg/L leaching from softening pellets, Ca-Al- CO_3 LDHs and the slag-based geopolymer, respectively. The PHREEQC calculation indicated that approximately 0.25% of the softening pellets dissolved. For struvite, the molar concentration of Mg^{2+} , NH_4^+ and PO_4^{3-} was 2.8, 1.4 and 2.3 mmol/L, respectively, which indicates the occurrence of dissolution of struvite. PHREEQC calculations indicated that this corresponds to approximate 1.5% of struvite dissolution.

For the three geopolymers, F^- leaching was detected, namely 1.3, 1.2 and 1.9 mg/L from slag-, fly ash- and metakaolin-based geopolymer respectively. This may influence the defluorination effect of geopolymers. Also, high concentrations of K^+ (1134 mg/L) and SO_4^{2-} (17.6 mg/L) were observed leaching from the slag-based geopolymer. From the fly ash-based geopolymer 23.5 mg/L PO_4^{3-} and 12.3 mg/L SO_4^{2-} were found to leach, which is undesirable from a drinking water supply perspective.

However, the consequence of the Ca^{2+} leaching (13.2mg/L) could have resulted in F^-

removal by precipitation of CaF_2 . PHREEQC calculations indicated that the precipitation of CaF_2 would occur for initial F^- concentrations over 12.9 mg/L. It is therefore hypothesized that the mechanism of F^- removal by Ca-Al-CO_3 LDHs, the slag-based geopolymer and softening pellets is sorption at low initial F^- concentrations, whereas precipitation plays a more prominent role at higher initial F^- concentrations.

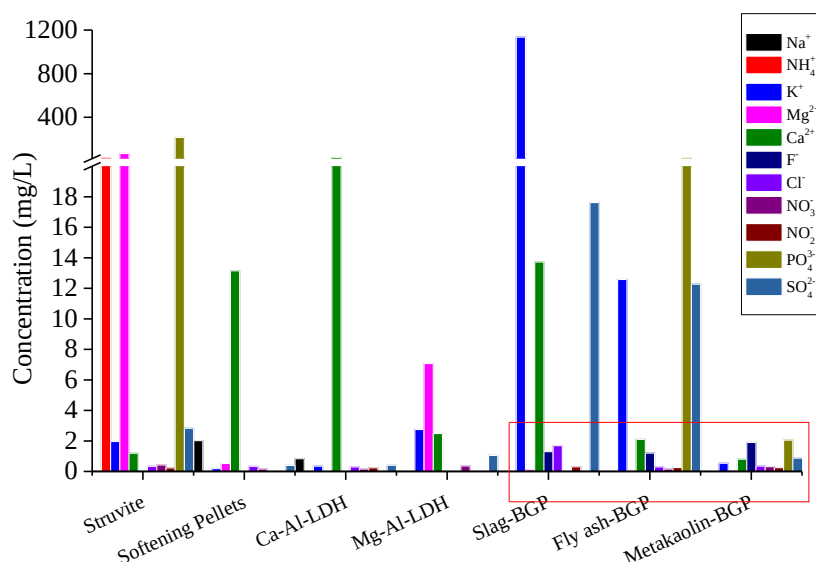


Figure 4. Ion leaching from low-cost mineral-based materials; Inset: F^- leaching from geopolymers. (BGP: based geopolymer)

4. Conclusions

A comparative assessment of low-cost materials from the perspective of their F^- removal capacity, structure and stability was performed. It can be concluded that Ca-based materials showed the strongest affinity for F^- (Ca-Al-CO_3 LDHs, slag-based geopolymer, softening pellets). The main mechanism of F^- uptake on Ca-Al-CO_3 LDHs, Mg-Al-Cl LDHs, slag-based geopolymers and softening pellets was found to be sorption at low initial F^- concentrations (<10 mg/L), whereas precipitation as CaF_2 is proposed to play a major role at higher initial F^- concentrations (>20 mg/L). Although the softening pellets had the highest Ca-content (96-97%; XRF), their dense structure and consequent low BET surface area (2-3 m^2/g), resulted in poorer performance than the Ca-based LDHs and slag-based geopolymers. Nevertheless, geopolymers, as well as struvite, should not be considered to be of interest for application in water treatment, as they would need modification due to their poor stability and/or F^- leaching.

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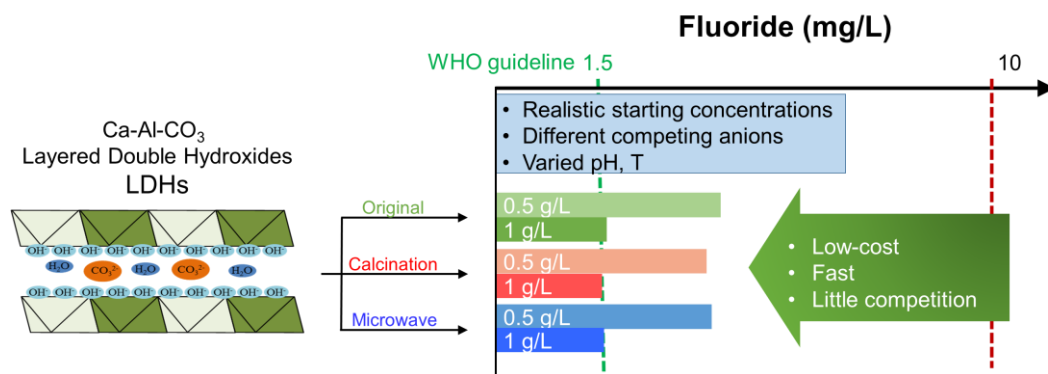
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Chapter 3

Fluoride removal by Ca-Al-CO₃ layered double hydroxides at environmentally-relevant concentrations



This chapter is based on:

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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., 2008b). Although a multitude of technologies such as coagulation, adsorption, ion exchange, electrochemical, and membrane processes have been investigated for 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., 2008b; Bhatnagar et al., 2011; Osterwalder et al., 2014). 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 (Kanno et al., 2014; Mohapatra et al., 2009).

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 $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} [A^{m-}_{x/m} \cdot nH_2O]$, 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., 2011a; Caporale et al., 2013a; Chitrakar et al., 2011; Das et al., 2006a; Halajnia et al., 2012a; Lazaridis et al., 2004a; Lv et al., 2009a; Pérez et al., 2006a). 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., 2011a; Lv, 2007a; Zhang et al., 2013). Thermal treatment using a muffle furnace (Lv, 2007a), 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 CO₂ 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., 2011a; Chang et al., 2011b; Du et al., 2014a; Kameda et al., 2015a; Lv et al., 2007a; Mandal and Mayadevi, 2008b; Wang et al., 2007). 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-CO₃ 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-CO₃ 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-CO₃ LDH modification methods with respect to their effect on LDH surface properties (including, XRD, FTIR, BET and p*H*_{zpc}).

2. Materials and methods

2.1 Chemicals and materials

All reagents including HCl, NaOH, NaF, NaCl, NaNO₃, NaHCO₃ and Na₂SO₄ were of analytical grade (Sigma-Aldrich). Deionized water was used throughout the experiments and treatment processes. Ca₄Al₂(OH)₁₂CO₃·*n*H₂O (*n*=4-5) LDH (ACTILOX[®]CAHC) was obtained from Nabaltec (Germany) with a Ca/Al ratio of 1.86. Before use, Ca-Al-CO₃ LDHs was dried in an oven at 105 °C for 12 h.

2.2 Calcination and microwave treatment of LDHs

The calcined Ca-Al-CO₃ LDHs were obtained by calcining Ca-Al-CO₃ 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-CO₃ 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-CO₃ 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-CO₃ 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-CO₃ 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-CO₃ LDH and its modified products were determined by N₂ 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-CO₃ 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-CO₃ 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 μ m). 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:

$$q = \frac{(C_0 - C)V}{m} \quad (1)$$

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.

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

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, 2011a). 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 (CaF₂) was carried out on PHREEQC (Dhiman and Keshari, 2006; Parkhurst and Appelo, 2013a). Detailed descriptions of simulation can be found in the SI.

3. Results and discussion

3.1 Characterization of Ca-Al-CO₃ LDHs

The differences in chemical and physical properties of untreated, calcined and microwave treated Ca-Al-CO₃ LDHs were compared by XRD, FTIR, and N₂ 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 $10 \text{ m}^2/\text{g}$, which is lower compared to other inorganic sorbents, such as activated alumina ($250 \text{ m}^2/\text{g}$) (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.

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

Sample	BET	Pore volume (cm^3/g)	Average pore diameter (nm)	pH_{PZC}
	Surface Area (m^2/g)			
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

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 (Ramirez-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 $\text{Al}(\text{OH})_3$ and CaCO_3 peaks was observed (Sun et al., 2017). Upon re-hydration, the peaks of 003 and 006 are usually re-occurring (Ramirez-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.

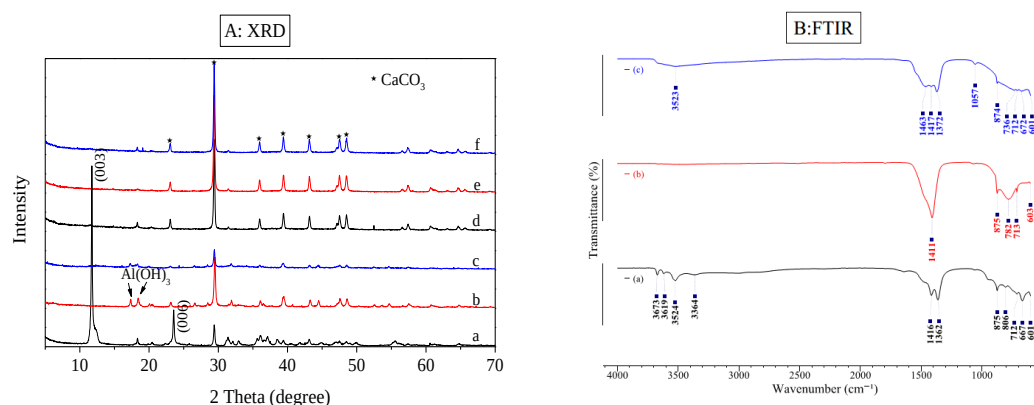


Fig. 1. XRD (A) and FTIR(B) spectra of Ca-Al- CO_3 LDHs (a), calcined Ca-Al- CO_3 LDHs (b) and microwave treated Ca-Al- CO_3 LDHs (c), Ca-Al- CO_3 LDHs after adsorption (d), calcined Ca-Al- CO_3 LDHs after adsorption (e) and microwave treated Ca-Al- CO_3 LDHs after adsorption (f); FTIR only measured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

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 (Cai et al., 2012; Lv et al., 2006b). The bands between 1000 and 600 cm^{-1} can be attributed to characteristic vibrations of calcium and aluminum oxides (Das et al., 2003; Lv et al., 2006b) (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 (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 ($105\text{ }^\circ\text{C}$) 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.

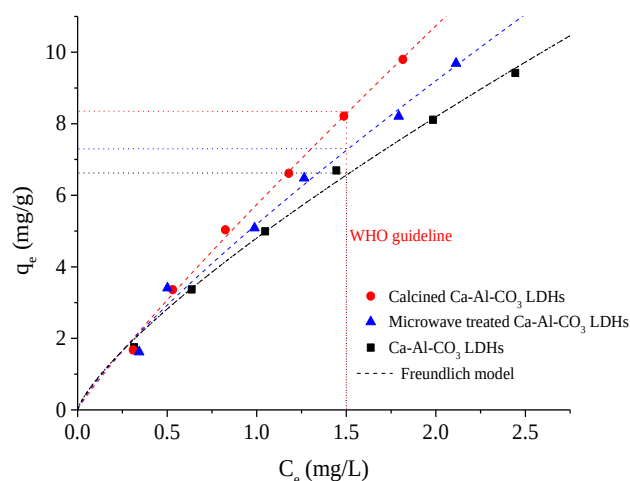


Fig. 2. F^- adsorption isotherm on Ca-Al-CO_3 LDH and its modified products, with loadings at WHO guideline of 1.5 mg/L value indicated as dashed lines.

(Initial F^- =2, 4, 6, 8, 10, 12 mg/L; pH=8; adsorbent dose=1 g/L; $T=25\pm 1\text{ }^\circ\text{C}$)

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., 2007a).

The equilibrium isotherms of F^- uptake on Ca-Al-CO_3 LDH and its modified products at different temperatures (12 ± 1 , 25 ± 1 and $35\pm 1\text{ }^\circ\text{C}$) 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).

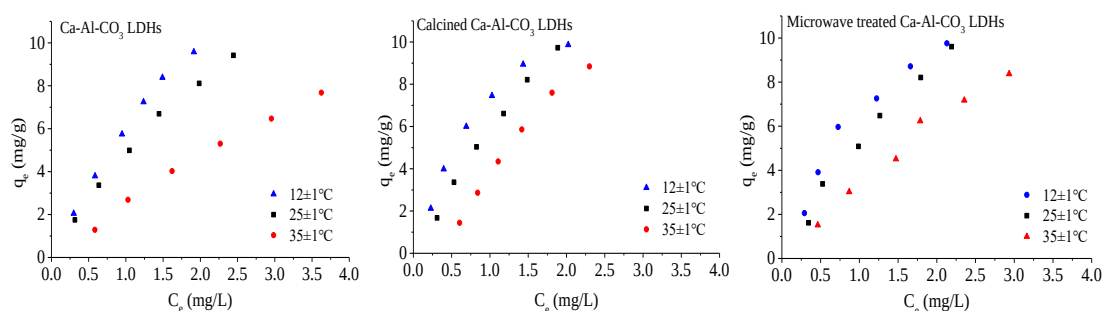


Fig. 3. Effect of temperature on the F^- removal by $Ca-Al-CO_3$ LDH and its modified products. (Initial F^- =2,4,6,8,10,12 mg/L; pH=8; adsorbent dose=1 g/L)

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).

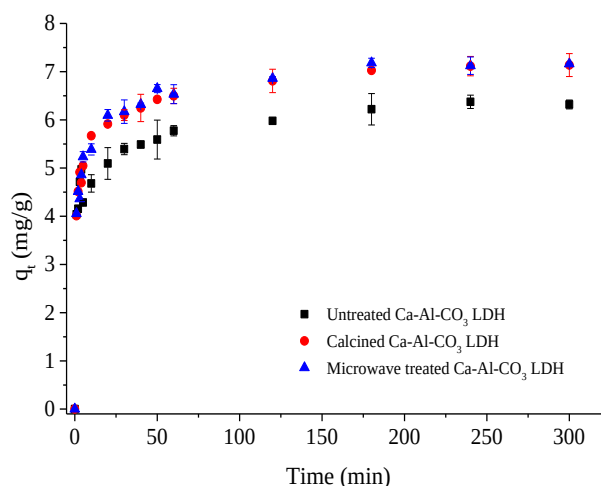


Fig. 4. The effect of contact time on F^- uptake by $Ca-Al-CO_3$ LDH and its modified products. (Initial F^- =10 mg/L; pH=8; adsorbent dose=1 g/L)

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 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; Tang and Zhang, 2016; Wang et al., 2017; Xiang et al., 2014). 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^- (Loganathan et al., 2013; Tang and Zhang, 2016). 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.

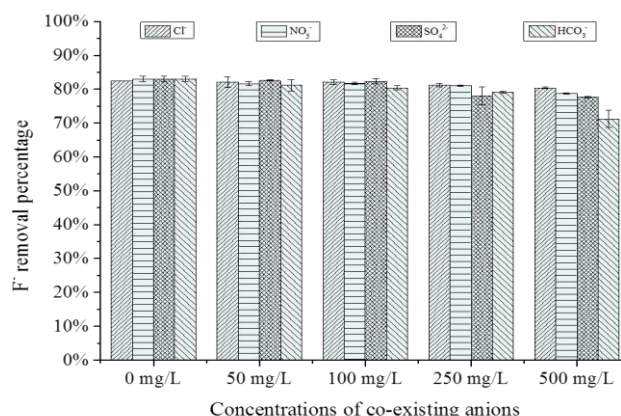


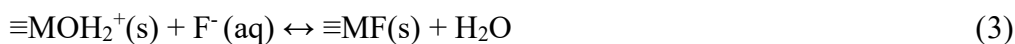
Fig. 5. Effect of co-existing anions on the F⁻ removal by unmodified Ca-Al-CO₃ LDH.
(Initial F⁻=10 mg/L; pH=8; adsorbent dose=1 g/L; T=25±1°C)

3.5 pH effect and buffering by LDHs

Ca-Al-CO₃ LDHs showed a noticeable effect on the pH of the solution. With the dose of 0.1-2 g/L, the unmodified Ca-Al-CO₃ 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-CO₃ 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-CO₃ LDH and its modified products over an initial pH range of 6-10. The Ca-Al-CO₃ 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 KMnO₄-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-CO₃ 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 ($\equiv M$) 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):



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 $HCO_3^- \rightleftharpoons CO_3^{2-}$ 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., 2007a). 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 into CO_2 during the calcination (Ramirez-Llamas et al., 2015).

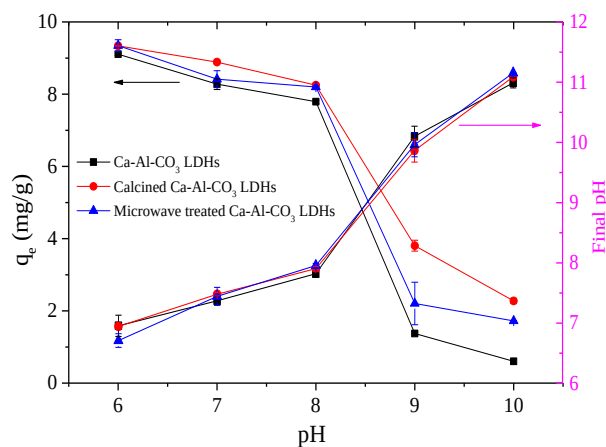


Fig. 6. Effect of initial pH on the F^- removal by Ca-Al- CO_3 LDH and its modified products.

(Initial F^- =10 mg/L; pH=6-10; adsorbent dose=1 g/L; $T=25\pm1^\circ C$)

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 ($<10 \text{ m}^2/\text{g}$) was lower than the surface areas obtained for Mg-Al- CO_3 LDHs ($196.8 \text{ m}^2/\text{g}$) (Batistella et al., 2011a), Zn-Al-Cl LDHs ($92.6 \text{ m}^2/\text{g}$) (Mandal and Mayadevi, 2009), Zn-Cr- NO_3 LDHs ($12\text{-}26 \text{ m}^2/\text{g}$) (Koilaraj and Kannan, 2013) and Li-Al LDHs ($37.24\text{-}51.27 \text{ m}^2/\text{g}$) (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 $F^-=6 \text{ mg/L}$, $\text{pH}=8$) for Ca-Al- CO_3 LDHs versus 1.84 mg/g (initial $F^-=5 \text{ mg/L}$, $\text{pH}=6$) 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^- ($1.33 \text{ \AA}$) (Shannon, 1976) is less than half the diameter of N_2 ($3.64 \text{ \AA}$) (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+} ($>10 \text{ mg/L}$) and F^- ($>4 \text{ mg/L}$) 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 $CO_3^{2-}\text{-}HCO_3^-$ 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 ($>\text{pH } 11$), which is undesirable from a removal capacity perspective. Achieving lower operating pH ($<\text{pH } 8$) 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-CO₃ LDHs can treat about 788 L of F⁻ contaminated water (initial F⁻=10 mg/L; pH=8; LDHs costs=€ 3.8-5.2 per m³ water; acidification costs=€ 200.7 per m³ 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. CaCO₃, 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-CO₃ LDH appears an attractive alternative for F⁻ removal.

4. Conclusions

Ca-Al-CO₃ 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-CO₃ 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 N₂. Given only marginal defluorination improvements by calcination/microwave treatment, applying untreated LDH appears to be the practically most feasible option. Competition with Cl⁻ and NO₃⁻ was not observed, whereas at higher HCO₃⁻ and SO₄²⁻ concentrations (>250 mg/L), a slight reduction in F⁻ removal was observed. It is recommended to further investigate Ca-Al-CO₃ 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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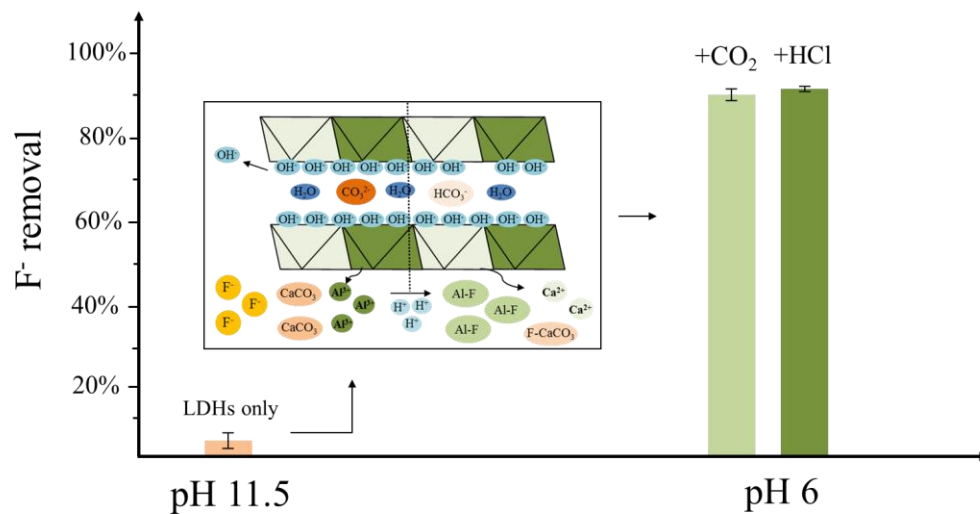
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Chapter 4

Fluoride removal from water by Ca-Al-CO₃ layered double hydroxides and simultaneous acidification



This chapter is based on:

Wei L., Zietzschmann F., Rietveld L.C., van Halem D. (2021) . Fluoride removal from water by Ca-Al-CO₃ layered double hydroxides and simultaneous acidification. Journal of Water Process Engineering, 40, 101957

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_2SO_4 , H_3PO_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 (Petersen and Lennon, 2010), however, exposure to excessive F^- concentrations can lead to dental and skeletal fluorosis (Kanduti et al., 2016). Over 200 million people worldwide are exposed to excessive concentrations of F^- from groundwater sources (Ayoob and Gupta, 2006). India and China are the worst affected, around 67 million and 41 million people are affected by fluorosis, respectively (Gupta and Ayoob, 2016). 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 (Ayoob et al., 2008b; Osterwalder et al., 2014). 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 (Cherukumilli et al., 2018).

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 (Sun et al., 2017). 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 (Batistella et al., 2011b; Reichle, 1986). 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 (Batistella et al., 2011b; Chang et al., 2011b; Du et al., 2014b; Kameda et al., 2015a; Lv et al., 2007a; Mandal and Mayadevi, 2008b; Wang et al., 2007). 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^- (Ghosal and Gupta, 2015), has recently shown promising defluoridation efficiency at low, environmentally relevant F^- concentrations (2-12 mg/L) (Wei et al., 2019) (Table 1). However, defluoridation by Ca-Al- CO_3 LDHs is highly pH sensitive, with better removals at pH 6-8 compared to $\geq$ 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 ($\sim$ 5%, pH=11.5, initial F^- =10 mg/L) (Wei et al., 2019).

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	(Wei et al., 2019)
Mg-Al-CO ₃	1.11	10	6	7.63*	(Lv et al., 2006a)
Ni-Al-NO ₃	2	10	6	4.82*	(Wang and He, 2014)
Zn-Al-Cl	4	10.2	6.2	1.9	(Mandal and Mayadevi, 2008a)
Mg-Al-CO ₃	2.5	5	6	1.84	(Wang et al., 2007)

*: kinetic model (Pseudo-second-order) value.

As a consequence, acidification is required, e.g. by hydrochloric acid (HCl), nitric acid (HNO₃) (Chi et al., 2017; Huang et al., 2015; Kang et al., 2018; Kim et al., 2013), or CO₂ (Cherukumilli et al., 2018; Li et al., 2012). However, potential effects of such acidification on Ca-Al-CO₃ 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 (Kameda et al., 2015a; Lv et al., 2007a). Considering the structural properties and the adsorption/ion exchange characteristics of LDHs, more examinations are needed to understand the possible negative impacts of applying Ca-Al-CO₃ LDHs in combination with acidification such as increased anion concentrations, competitive adsorption, and modifications/changes to the structure of Ca-Al-CO₃ 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-CO₃ 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-CO₃ LDHs.

2. Materials and methods

2.1 Chemicals and Materials

All reagents including NaF, HCl, HNO₃, H₂SO₄, and H₃PO₄ 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 $Ca_4Al_2(OH)_{12}CO_3 \cdot nH_2O$ ($n=4-5$) 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 Figure 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 ~15min) using various acids (1M HCl, 1M HNO_3 , 0.5M H_2SO_4 , 0.33M H_3PO_4) or by injection of CO_2 with a flow of 5mL/min (10min), respectively (acid doses recorded), and stirring for 24 h (enough to reach equilibrium based on previous studies (Lv et al., 2007a; Wei et al., 2019)) 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 10000 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. Figure 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 Figure 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 Figure 1). The solutions were stirred for 3 h under pH 6 with a cap on the jars (1L) 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 12h, then cooled and ground into powder for further use.

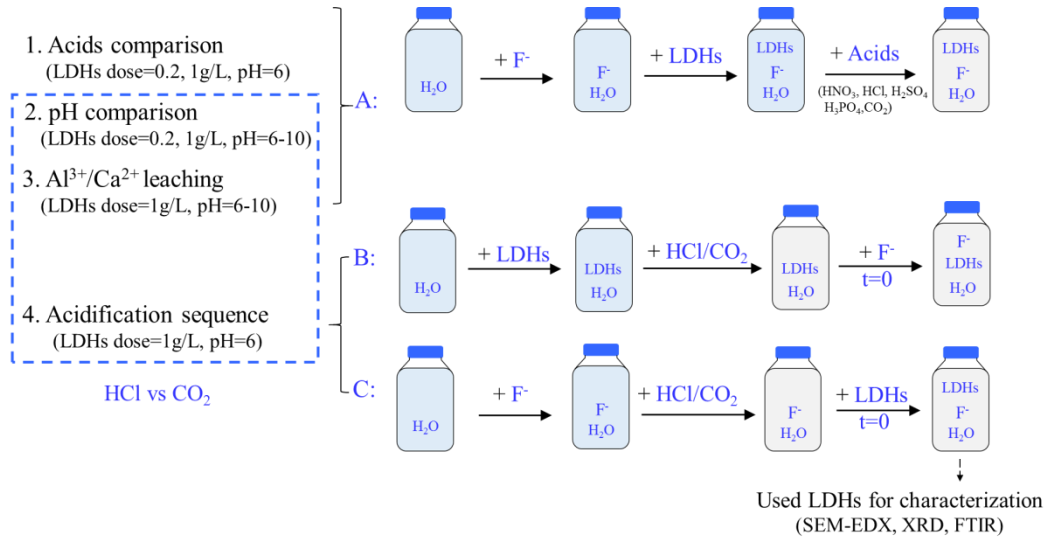


Figure 1. Overview of experimental conditions and procedures.

2.3 Analytical methods

Scanning electron microscope (SEM) images and X-ray analyses (EDX) of Ca-Al-CO₃ 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⁻, NO₃⁻, SO₄²⁻, PO₄³⁻ and HCO₃⁻ were analyzed by Ion chromatography (IC) (Metrohm 881, Switzerland) with a column of Mestrosep A Supp 5 and ICE-99-9860, respectively. Concentrations of Ca²⁺ and Al³⁺ leaching after experiment were measured by ICP-MS (Analytik Jena AG, Germany).

2.4 Data evaluation and modelling

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

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

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 (Dhiman and Keshari, 2006; Parkhurst and Appelo, 2013a). 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- CO_3 LDHs at 0.2 and 1 g/L from solutions adjusted to pH 6 by acidification with various acids are shown in Figure 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) (Cai et al., 2012; Das et al., 2003; Lv et al., 2007a), and much lower than that on Indian Bauxite (12-77 g/L) (Cherukumilli et al., 2018). A pH of 6 was chosen to reach well-discernible results and because substantial benefits of lower pH were observed previously (Das et al., 2003; Lv et al., 2007a; Wei et al., 2019). Under acidified conditions the removal reached 37% (CO_2) and 64% (HCl) at a 0.2 g/L LDHs dose, 90% (CO_2) and 94% (HCl) at 1 g/L LDHs. At the lower LDHs dose, acidification by HNO_3 resulted in a similar F^- removal as HCl, whereas for H_3PO_4 , H_2SO_4 , 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 NO_3^- (Kang et al., 2018). 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 $\geq 90\%$.

The high pH buffering capacity of Ca-Al- CO_3 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 CO_2 (~0.99 g/L) is much lower than the reports by Cherukumilli et al. (22.5-34.7 g/L) (Cherukumilli et al., 2018) and Li et al. (80.1 g/L) (Li et al., 2012), although the amount of acids is usually not reported (Chi et al., 2017; Huang et al., 2015; Kang et al., 2018; Kim et al., 2013). The consequent anion concentrations (Cl^- , NO_3^- , PO_4^{3-} , SO_4^{2-} and HCO_3^-) at 1 g/L LDHs are given in Figure 2B, at

the start and end of the experiments, respectively. The consequent concentrations of NO_3^- , SO_4^{2-} and PO_4^{3-} were much higher than the drinking water threshold (cf. Table S3), whereas the concentrations of Cl^- and HCO_3^- were thought to be acceptable because although excessive Cl^- concentrations ($> 250 \text{ mg/L}$) is detectable by taste, a guideline value for Cl^- in drinking water is not established, and HCO_3^- is not proposed as a chemical related to taste or odour in drinking water (Mueller and Helsel, 1996; World Health Organization, 2011). The NO_3^- concentration, after dosing HNO_3 , was 835 mg/L and decreased only slightly during the experiments (829 mg/L). At lower Ca-Al- CO_3 LDHs dose (0.2 g/L), NO_3^- concentration was still high ($\sim 170 \text{ mg/L}$). The PO_4^{3-} concentrations, after dosing H_3PO_4 , decreased from 795 to 238 mg/L during the experiments, and SO_4^{2-} concentrations, after dosing H_2SO_4 , decreased from 671 to 618 mg/L . These results indicate a partial uptake of PO_4^{3-} and SO_4^{2-} by Ca-Al- CO_3 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 (Lv et al., 2007a), then for monovalent ions. The high uptake of PO_4^{3-} could also be due to the formation of Ca- PO_4 precipitate (SI of Hydroxyapatite=6.31 calculated by PHREEQC at pH6) under such condition (Kanno et al., 2014). HCl acidification resulted in $\sim 450 \text{ mg/L}$ Cl^- and the concentration of introduced HCO_3^- , after dosing CO_2 , was approximately 550 mg/L at 1 g/L LDHs.

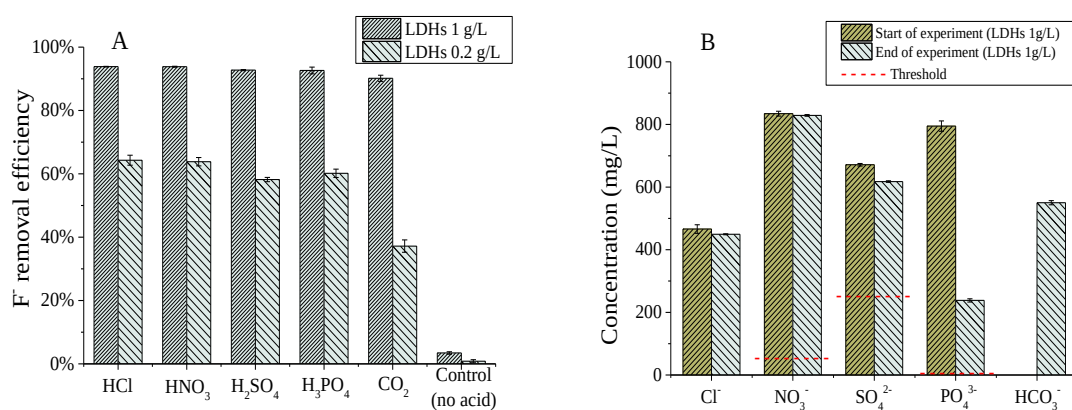


Figure 2. (A) F^- removal efficiency at 0.2 and 1 mg/L LDHs dose, and (B) anion concentration of different pH-adjusting acids at start and end of the experiment. Initial $\text{F}^- = 10 \text{ mg/L}$, initial $\text{pH} = 6$, $T = 22 \pm 1^\circ\text{C}$, LDHs dose = 0.2 or 1 g/L .

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

While considerable differences were not discernible between HCl and CO_2 acidification

at the high LDHs dose, F^- removal was slightly higher for HCl than for CO_2 at the lower LDHs doses at pH 6 and 7; at higher pH, no differences appeared (Figure 3A). Overall, F^- removal increased with decreasing pH, and the effect was more pronounced for HCl than for CO_2 acidification, possibly due to competition by HCO_3^- . Upon application of CO_2 , HCO_3^- 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 HCO_3^- concentrations (>250 mg/L); such an adverse effect was not observed for Cl^- as a competitive anion (Wei et al., 2019).

The F^- removal by 0.2 and 1 g/L Ca-Al- CO_3 LDHs at varying initial F^- concentrations are shown in Figure 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 CO_2 , especially at the lower LDHs dose (0.2 g/L), likely confirming potential adverse competitive effects of HCO_3^- (cf. 3.1). At the Ca-Al- CO_3 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 CO_2 , 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- CO_3 LDHs dose of 1 g/L (Figure S4).

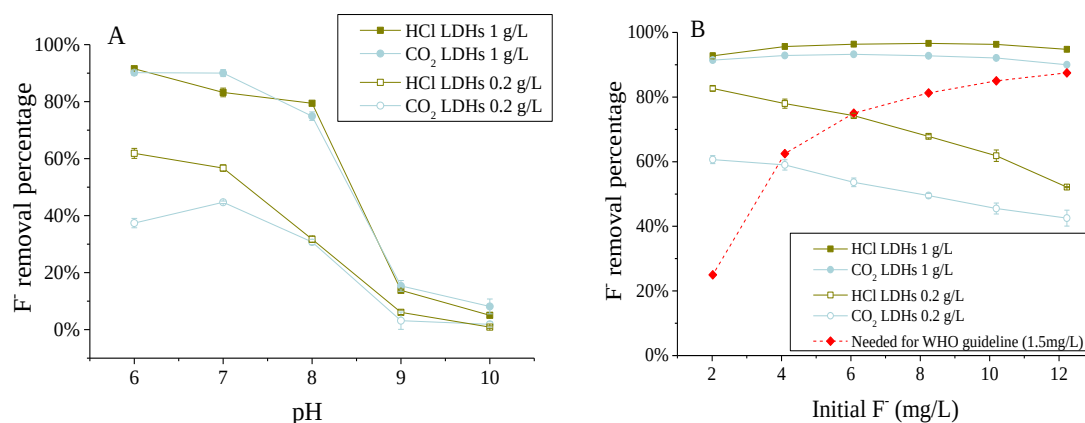


Figure 3. The effect of pH (A) (Initial F^- =10 mg/L; pH=6, 7, 8, 9, 10; LDHs dose=0.2 g/L; $T=22\pm1^\circ C$) and initial F^- (B) (LDHs Initial F^- =2,4,6,8,10,12 mg/L; pH=6; LDHs dose=0.2 or 1 g/L; $T=22\pm1^\circ C$) on F^- removal by Ca-Al- CO_3 .

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-CO₃ LDHs-containing suspension (cf. Figure 1). The absolute and relative F⁻ removal is depicted over time for the two tested acidification orders with HCl and CO₂, respectively, in Figure 4. Several models fit to the kinetic experimental data and are presented in the supplementary information. HCl acidification resulted in faster removal kinetics than CO₂ acidification. Specifically, equilibria were reached after 20 min, 60 min, 90 min, >180 min for HCl + F⁻ before/after and CO₂ + 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-CO₃ LDHs surfaces were firstly activated by acids when acidified (prior to F⁻ addition) and simultaneously occupied by respective anions (Cl⁻ and HCO₃⁻), which subsequently had to be replaced when F⁻ was added. The effect was particularly pronounced for CO₂, 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 HCO₃⁻ were more pronounced than with the other ions. When CO₂ is diffusing into the solution, the hydration of CO₂ can occur in two paths. At pH>10, the predominant mechanism is via direct reaction with OH⁻ forming HCO₃⁻ and CO₃²⁻ (instantaneous); At pH<8, the direct hydration is the predominant mechanism forming H₂CO₃ and HCO₃⁻ (instantaneous) (Danckwerts and Kennedy, 1958; Kern, 1960) and resulting in a high concentration of HCO₃⁻ which has an adverse effect on F⁻ removal (Wei et al., 2019). 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 HCO₃⁻ can be formed because of the dissolution of LDHs after HCl acidification, no adverse effect was observed at this concentration (Wei et al., 2019).

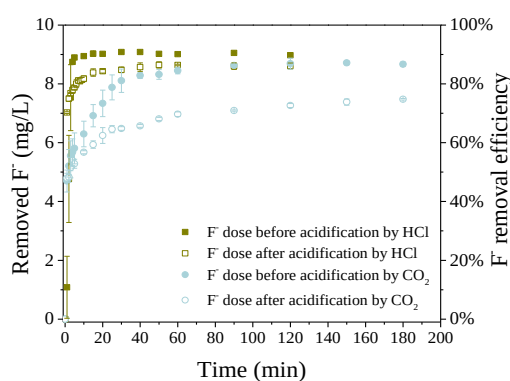


Figure 4. F⁻ removal capacity and removal percentage, as a function of time. Initial F⁻=10 mg/L; pH=6; LDHs dose=1 g/L; T=22±1 °C.

3.4 Al³⁺ and Ca²⁺ leaching

Figure 5 shows the Al³⁺ and Ca²⁺ concentrations after addition of 1 g/L Ca-Al-CO₃ LDHs. The concentration reached ~70 mg/L for both Al³⁺ and Ca²⁺ without pH control (pH=11.5). After HCl acidification, Al³⁺ concentrations ranged between 0.05 mg/L (pH 6) and 75 mg/L (pH 10) and Ca²⁺ concentrations ranged between 184 mg/L (pH 9) and 273 mg/L (pH 6). During CO₂ acidification, Al³⁺ concentrations were in the range of 0.12 mg/L (pH 6) to 54 mg/L (pH 10), and Ca²⁺ ranged from 35 mg/L (pH 9) to 241 mg/L (pH 6). CO₂ acidification thus caused slightly higher Al³⁺ leaching at pH below 9 but less Ca²⁺ leaching compared to HCl. Ca²⁺ concentrations were within the ranges of the WHO (100-300 mg/L), however, occasionally additional Ca²⁺ removal could be needed if this water is distributed for drinking water supply (World Health Organization, 2011). The observed Al³⁺ and Ca²⁺ leaching indicates the dissolution of Ca-Al-CO₃ LDHs. Based on its formula Ca₄Al₂(OH)₁₂CO₃·nH₂O (n=4-5) and the measured concentrations of Ca²⁺, approximately 24% of Ca-Al-CO₃ 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 CO₂ acidification, respectively.

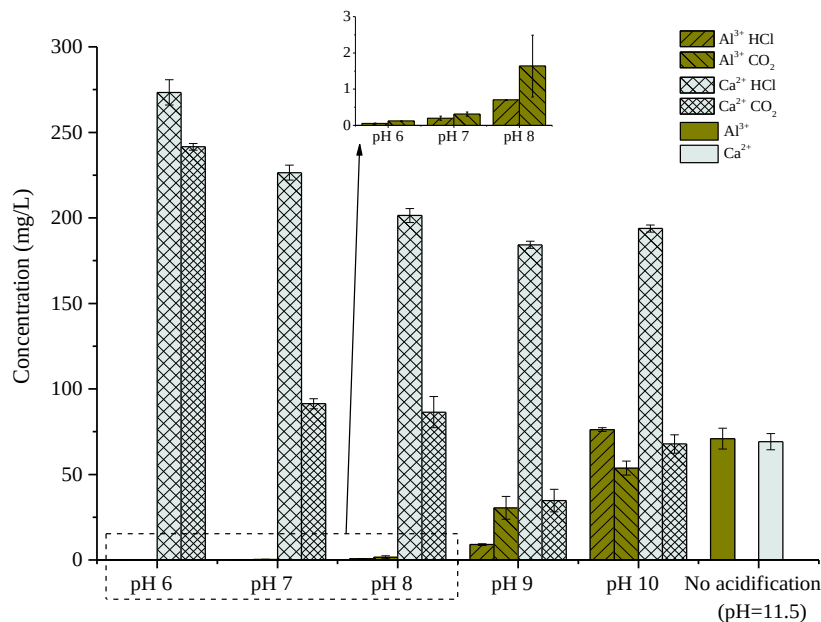


Figure 5. Al³⁺ and Ca²⁺ leaching from Ca-Al-CO₃ LDHs under different pH conditions; inset: Al³⁺ concentrations for pH 6, 7, 8. Initial F=10 mg/L, T=22±1 °C, LDHs dose=1 g/L.

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 ($\alpha\text{-Al}(\text{OH})_3$) and boemite ($\gamma\text{-AlOOH}$) to amorphous Al species with decreasing pH from 11 to 6 (Du et al., 2009). F^- removal from solution onto such precipitates was previously observed (He et al., 2015; Lu et al., 2000a).

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

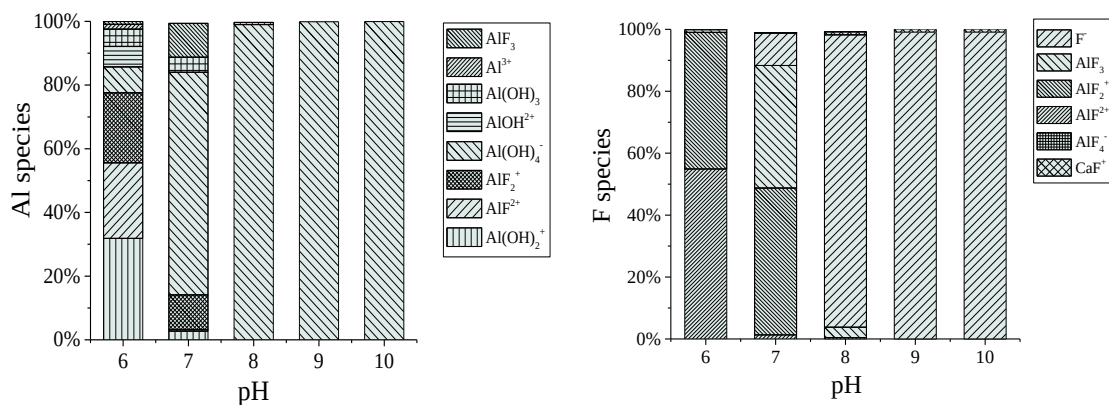


Figure 6. Distribution of Al and F species under different pH conditions simulated by PHREEQC. $T=25^\circ\text{C}$, $\text{pH}=6\text{--}10$, $\text{F}^-=10\text{ mg/L}$, the molar ratio of $\text{F}^-/\text{Al}^{3+}=0.2$.

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 from F/Ca. According to PHREEQC modelling and literature data, the various Al-containing species such as $\text{Al}(\text{OH})_2^+$, AlF^{2+} , AlF_2^+ , $\text{Al}(\text{OH})_4^-$, etc. were present under the tested conditions, particularly when lowering the $\text{pH} < 8$, likely serving as adsorption/complexation/interaction partners for F^- , depending on the respective pH and $\text{F}^-/\text{Al}^{3+}$ ratio (Bi et al., 2004; Deng et al., 2011; Liu et al., 2013) (Figure 7). But specifically for CO_2 acidification, F^- can also be removed by CaCO_3 adsorption (Budyanto et al., 2015).

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.

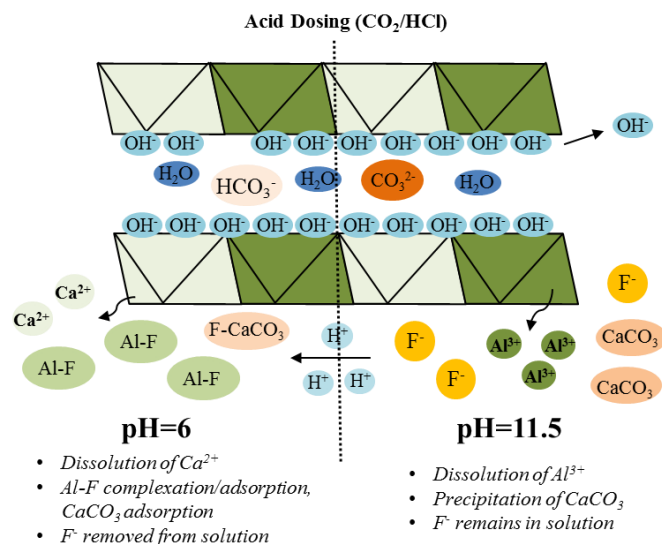


Figure 7. Schematic drawing of proposed dissolution-complexation/adsorption mechanism.

3.6 Characterization of Ca-Al- CO_3 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 Figure 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 Figure 8A. The virgin LDHs show sharp and symmetric characteristic peaks (003 and 006) of hydrotalcite-like compounds at lower 2θ values (Cavani et al., 1991), 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 (Cai et al., 2012; Kameda et al., 2015a; Lv, 2007a). 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 $\text{Al}(\text{OH})_3$. The aqueous stability of LDHs is driven by

the solubility of the corresponding divalent metal salt (Allada et al., 2002; Bravo-Suárez et al., 2004). The damage of the layered hydrotalcite-like structure after acidification indicated a low stability of Ca-Al-CO₃ LDHs.

The FTIR spectra of Ca-Al-CO₃ LDHs before and after the experiments are shown in Figure 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 (Noorjahan et al., 2015), sorbed CO₂ and interlamellar CO₃²⁻ at 1419 and 1363 cm⁻¹ (Cai et al., 2012; Lv et al., 2006b), as well as calcium and aluminum oxides at 1000 and 600 cm⁻¹ (Das et al., 2003; Lv et al., 2006b)). Structural changes by CO₂ 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 CO₂ injection likely inhibited the dissolution of CaCO₃ (cf. Figure S6) and probably led to the formation of Al(OH)₃ due to the weak acid property of H₂CO₃ (Hem and Roberson, 1967). Adsorbents with a high defluoridation capacity are often double or triple metal oxides, while they are generally amorphous and show increased performance at lower pH (<7) (Han et al., 2010; Wang et al., 2017; Wu et al., 2007; Yang et al., 2015). The main mechanism of F⁻ uptake by Mg-Al LDHs (Mg-Al-NO₃ and Mg-Al-Cl LDHs) has been previously proposed as the result of exchange between aqueous F⁻ and NO₃⁻ or Cl⁻ anions positioned in the Mg-Al LDHs interlayer (Kameda et al., 2015). However, our proposed removal mechanism is F⁻ adsorption or complexation onto/into Al-containing species and CaCO₃ (in the case of CO₂ 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 CaCO₃ (in the case of CO₂ 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.

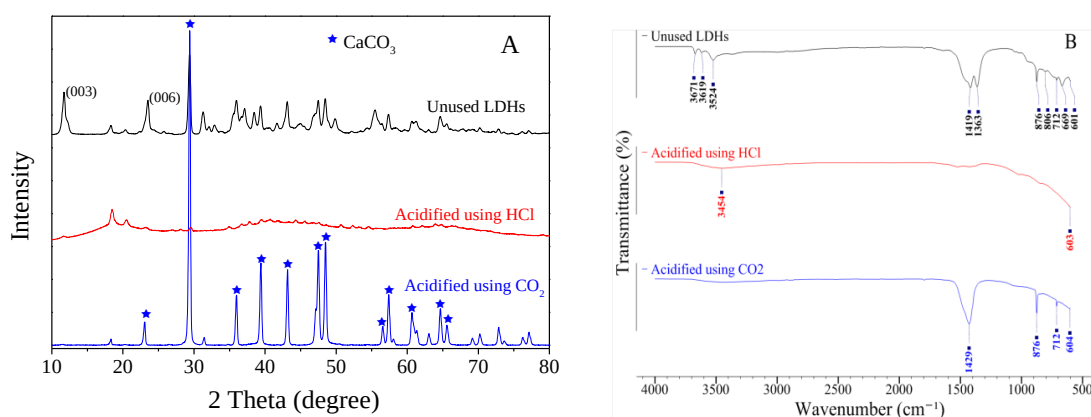


Figure 8. XRD patterns (A) and FTIR spectra (B) of the Ca-Al-CO₃ LDHs before and after experiments.

4. Conclusions

In the present work the effects of pH-adjusting acids on F⁻ removal from water by Ca-Al-CO₃ LDHs were reported. Acidification by conventional acids like HCl or CO₂ led to a substantially increased performance of Ca-Al-CO₃ 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 CO₂ were 62 and 92% (HCl), and 38 and 90% (CO₂) at LDHs doses of 0.2 and 1 g/L, respectively. Addition of HCl and CO₂ 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-CO₃ 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 CO₂ as the acidification method in combination with Ca-Al-CO₃ LDHs. The reusability and feasibility of Ca-Al-CO₃ LDHs in column and real groundwater should be examined in future studies.

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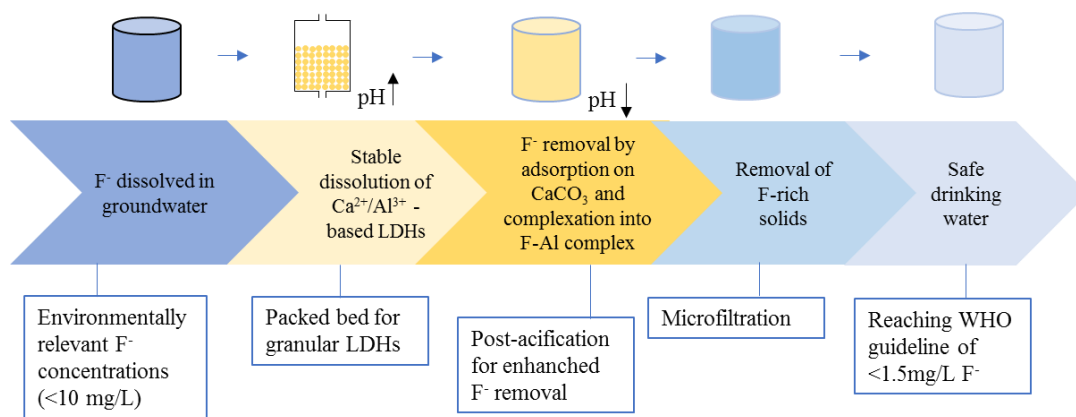
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Chapter 5

Defluorination using packed bed granular Ca-Al-CO₃ layered double hydroxides with CO₂-based post-acidification and microfiltration



This chapter is based on:

Wei L., Zietzschmann F., Rietveld L.C., van Halem D. Fluoride removal by packed bed granular Ca-Al-CO₃ layered double hydroxides with CO₂-based post-acidification and microfiltration (in preparation).

Abstract

Powdered layered double hydroxides (LDHs) have been shown to efficiently remove fluoride (F^-) from groundwater, particularly at relatively low pH (<7). However, F-containing groundwater typically has a higher pH, making it is critical for application to apply acidification. Therefore, this study investigated the combination of granular Ca-Al- CO_3 LDHs packed beds with CO_2 -based post acidification and microfiltration. This allows for sequential dissolution and precipitation of LDH-sourced calcium (Ca^{2+}) and aluminum (Al^{3+}), removed by a microfiltration step. We found that F^- removal was effective with CO_2 post-acidification from 5 mg F^- /L to below the WHO standard of 1.5 mg/L. F^- removal capacity was found to be exceeding 30.46 mgF/gLDHs and 15.06 mgF/gLDHs, for batch and column mode, respectively. The column study demonstrated a slow and stable LDHs dissolution rate of 0.23g/L, leading to continuous and efficient F^- removal. Solids characterization by XRD confirmed precipitation of dissolved granular LDHs as particulates ($CaCO_3$ and hydrated Al oxides).

1. Introduction

Excessive fluoride (F^-) intake causes dental and skeletal fluorosis. The F^- removal from groundwater has been an engineering challenge for a long time, and many efforts have been made to develop effective defluorination technologies (Ayoob et al., 2008b; Osterwalder et al., 2014). Layered double hydroxides (LDHs) are a family of anionic clays that have been considered applicable in F^- removal due to their high defluorination capacity and cost-effectiveness (Sun et al., 2017). Considering the affinity of Ca^{2+} and Al^{3+} towards F^- (Ghosal and Gupta, 2015), Ca-Al- CO_3 LDHs has been recently studied and shown promising defluorination efficiency at low, environmentally relevant F^- concentrations (2-12 mg/L) (Wei et al., 2019). To enhance F^- removal capacity and reach the WHO guideline (1.5 mg/L) at environmentally relevant F^- , it was found that acidification with HCl or CO_2 was an effective method (Wei, 2019, 2020). It was found that dissolution of LDH would offer opportunities for subsequent F^- precipitation/complexation with either Ca^{2+} or Al^{3+} . This novel sequence (Figure 1) has potential for application in water supply, however, it is then key to move towards a continuous flow system, which would require granulated Ca-Al- CO_3 LDHs instead of powder.

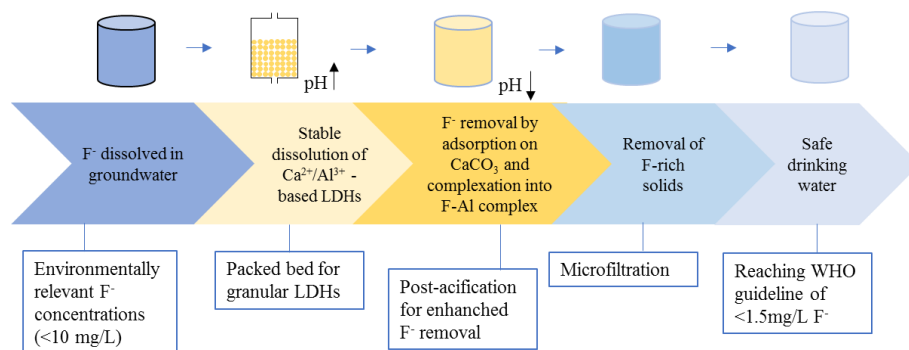


Figure 1. Schematic overview of F^- removal by the sequence of granular Ca-Al- CO_3 LDH packed bed with post acidification and microfiltration.

Double or triple metal oxides have been widely tested as high defluorination adsorbents, while they are generally amorphous and show increased performance at lower pH (<7) (Han et al., 2010; Wang et al., 2017; Wu et al., 2007; Yang et al., 2015). Aluminum (hydrate) oxides can be used for F^- removal, but the addition of a large amount of acid and alkali is required to make Al hydrated, and the amorphous state of the product causes separation difficulties (He et al., 2015), making its application in drinking water treatment challenging. For Ca-Al- CO_3

LDHs, however, the dissolution with the release of Ca^{2+} , Al^{3+} , OH^- and CO_3^{2-} creates excellent conditions for F^- removal. On the one hand, F^- can be adsorbed onto the precipitate of CaCO_3 (Budyanto et al., 2015). On the other hand, F^- can be removed by adsorption or complexation onto/into various rehydrated Al oxides which re-precipitated when acidifying (Wei et al. 2020). CO_2 is much cheaper than HCl and it does not lead to the introduction of potentially harmful or undesired anions (Wei et al. 2020). The granular Ca-Al- CO_3 LDHs packed bed with CO_2 -based post acidification makes it possible to remove F^- continuously and efficiently.

A commonly used granulation method is impregnation load by supporting an active component such as a metal oxide on a core carrier (García-Sánchez et al., 2013). Molding and calcination is another conventional granulation method that has been used in the zeolite, which requires several hours at high temperature resulting, making it a time and energy intensive process (Pavlov et al., 2015). Alginate is a water insoluble gel that has attracted much attention on account of its biocompatible and biodegradable property, and rapid gelation ability in many fields. Alginate gelation occurs when divalent cations (Ca^{2+} , Fe^{3+} , Al^{3+} , Zr^{4+}) interact with blocks of G residues, divalent ions diffuse into the sodium alginate solution and replace Na^+ with a rapid, strong and irreversible formation of gel.

Therefore, the main objectives of this paper are to i) investigate the dissolution and F^- removal performance of the granulated Ca-Al- CO_3 LDHs (extrusion granules and dropping beads) using sodium alginate as the gel; ii) investigate the feasibility and the defluorination performance of packed bed with granulated Ca-Al- CO_3 LDHs with post-acidification and microfiltration.

2. Materials and methods

2.1 Materials

All reagents including NaF, HCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, sodium alginate 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. A 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 $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot n\text{H}_2\text{O}$ ($n=4-5$) 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 remove any previously adsorbed water.

2.2 Preparation of granular Ca-Al-CO₃ LDHs

Sodium alginate was dissolved in deionized water at 1-10 wt% concentrations at 60°C. The Ca-Al-CO₃ LDHs granules were prepared in two methods, extrusion and dropping. For the method of extrusion (Figure 2A) (Wu et al., 2013), 5g of Ca-Al-CO₃ LDHs powder and sodium alginate solution (1-10 wt%, 5-15mL) as a binder were combined. After 24h of standing, the wet mass was granulated to cylinder-shaped granules using a syringe and dried in an oven at 65°C for 24h. The dried cylindrical granules were broken up manually into short rods (3.0-5.0 mm) yielding extrusion granules with the Ca-Al-CO₃ LDHs content of 54%-99%. For the method of dropping (Figure 2B) (Phuong, 2014), the desired amount of Ca-Al-CO₃ LDHs was added into a sodium alginate solution (2 wt%, 5 mL) under intensive mixing. The suspension contained in the plastic syringe was dropped to a CaCl₂ solution (3 wt%, 500 mL) to form spherical beads. After curing in the same CaCl₂ solution for 12 h, the beads were rinsed with deionized water 3 times to remove excess Ca²⁺ and dried in an oven at 65°C for 24h yielding dropping beads with the Ca-Al-CO₃ LDHs content of 0%, 33%-83%.

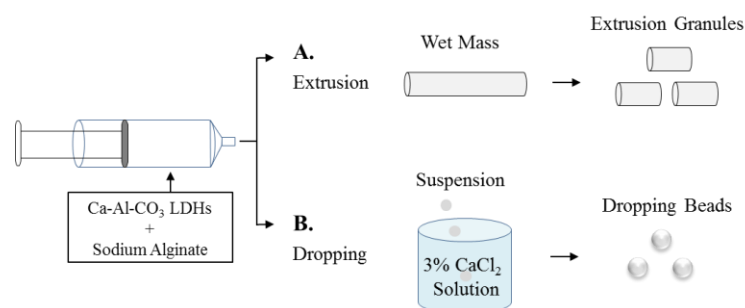


Figure 2. Steps taken to granulate Ca-Al-CO₃ LDHs with sodium alginate by means of extrusion (A) and dropping (B).

2.3 Batch experiments

The dissolution of LDHs results in the leaching of cations (Ca²⁺ and Al³⁺) and anions (CO₃²⁻ and OH⁻) and leads to an increase of the pH of the solution. The dissolution equilibrium time was found to be ~30h in the preliminary batch experiment based on Ca²⁺ and pH (Figure S1). The dissolution of the extrusion granules (54%-99% LDHs) and dropping beads (0%, 33%-83% LDHs) was tested by investigating Ca²⁺ and Al³⁺ leaching. 0.1 g sample was firstly soaked in 100 mL deionized water for 30 h on a shaker with a speed of 120 rpm at room temperature (22±2°C). The pH of the solution was recorded and a 3 mL sample was filtered by 0.1 µm membrane for the analysis of Ca²⁺ and Al³⁺ concentrations at this pH. Then

the pH of the solution was adjusted to 7 using 0.1 M HCl and a 10 mL sample was filtered by 0.1 μm membrane for the analysis of Ca^{2+} and Al^{3+} concentrations at pH 7 to investigate the effect of pH on their concentrations. For dropping beads, the above process was repeated to investigate the influence of CaCl_2 solution on Ca^{2+} concentration.

The effect of LDHs content in the produced granules and pH was examined in batch experiments. 0.1g of extrusion granules or dropping beads were soaked in 100 mL water (initial $\text{F}^- = 10\text{mg/L}$) on a shaker (120 rpm) for 30h. Then samples (3 mL each) were taken for F^- , Ca^{2+} , Na^+ and Al^{3+} measurement. The pH of the solutions was adjusted using 0.1 M HCl to 7, samples (3 mL each) were taken for F^- , Ca^{2+} , Na^+ and Al^{3+} measurement after 1h. In a similar manner, different pHs (6, 7, 8, 9, 10) by using 0.1 M HCl or bubbling CO_2 (4 mL/min) were compared at an initial F^- concentration of 10 mg/L (100 mL). The F^- removal capacity (q_e : mg/g) of the granules was calculated using the formula:

$$q_e = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

where C_0 (mg/L) and C_e (mg/L) are initial and equilibrium (soaked 30 h for high pH, 1 additional hour for pH 7) F^- concentrations, respectively; V (L) is the initial volume of solution, and m (g) is the mass of the granules.

To investigate the weight loss and F^- removal performance of the granules during the experimental cycles, 1g of extrusion granules (95% LDHs) was dosed to 1 L of 10 mg F^- /L solution and soaked for 30 h on a shaker with 120 rpm. A 10 mL sample was taken and filtered by 0.1 μm membrane for Ca^{2+} and Al^{3+} measurement. Then the pH of the solution was adjusted to 7 using 0.1 M HCl. After 1h, a 10 mL sample was taken and filtered by 0.1 μm membrane for Ca^{2+} and F^- measurement. Another 10 mL sample was taken and filtered by a 0.1 μm membrane for Al^{3+} analysis. The used extrusion granules were washed and filtered by 0.1 μm membrane, then dried at 65 $^\circ\text{C}$ for 12 h and weighed. The above process was repeated twice.

2.4 Column study

Perspex columns with an inner diameter of 1 cm and a height of 20 cm were used to evaluate the F^- removal performance of extrusion granules (Figure 3). The column was packed with 4 g of extrusion granules (95%) with a bed height of 10 cm. The packed column was flushed upwards using deionized water at the flow rate of 0.5 mL/min by a peristaltic pump for 2h to establish a steady state flow condition. The dissolution amount of the granules

during the 2h flushing was less than 1%, which was ignored. Then the F^- solution (5mg/L) was introduced to the packed column at the same flow rate. The empty bed contact time (EBCT) (=fixed-bed volume/flow rate) was 15.7 min. Samples (10 mL) were taken from the outlet of the column at regular time (2, 4, 6, 8, ..., 166h) intervals and the pH was adjusted to 7 by bubbling CO_2 into the outlet tank of the column, then filtered using 0.1 μm membrane for F^- , Ca^{2+} and Al^{3+} measurement.

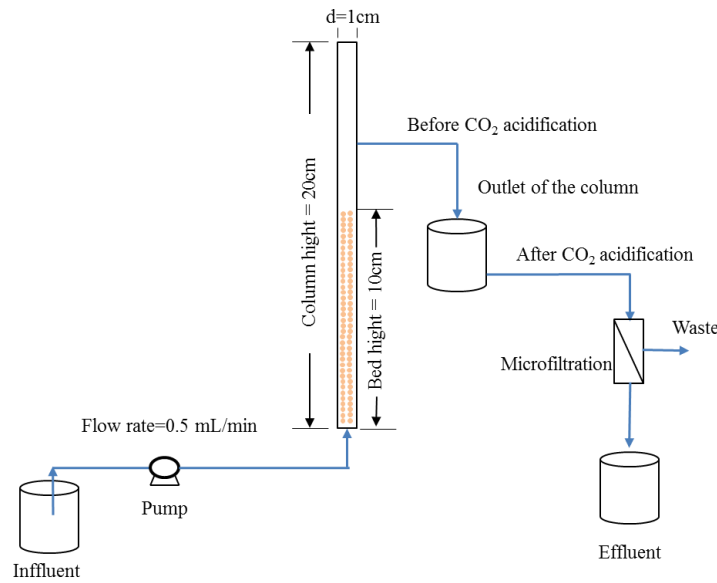


Figure 3 Experimental set-up of F^- removal by packed bed granular Ca-Al- CO_3 LDHs with post-acidification and microfiltration.

2.5 Instrumental and data analysis

The crystalline structure of the samples before and after experiments was characterized using an X-ray Bruker D8 Advance diffractometer (Bruker). The concentrations of F^- , Cl^- and Ca^{2+} were analyzed by Ion chromatography (IC) (Metrohm 881 and 883, Switzerland) with a column of Mestrosep A Supp 5 and Mestrosep C6-150/4.0, respectively. Concentrations of Al^{3+} were measured by inductively coupled plasma mass spectrometry (ICP-MS) (Analytik Jena AG, Germany).

In the batch experiments, the dissolution percentage of LDHs (%) can be determined based on LDHs' formula $Ca_4Al_2(OH)_{12}CO_3 \cdot nH_2O$ ($n=4-5$) and Ca^{2+} concentration at pH 7, as follows:

$$\text{The dissolution percentage of LDHs} = \frac{C_{Ca^{2+}, pH7}}{C_T \times P} \times 100, \quad (2)$$

where C_T (mg/L) is the total concentration of Ca^{2+} if all of the dosed LDHs dissolved; P (%)

is the mass fraction of LDHs.

In the column study, the dissolved LDHs (mg/L) can be determined as follows:

$$\text{The dissolved LDHs} = \left(\frac{C_{t,pH7}}{40 \text{ g/mol}} \div 4 \right) \times M_L, \quad (3)$$

where $C_{t,pH7}$ is the concentration of Ca^{2+} in the effluent at time t after CO_2 acidification (mg/L); M_L is the molar mass of LDHs (g/mol). The total dissolved LDHs (g) can be quantified, as follows:

$$\text{The total dissolved LDHs} = \frac{1}{1000} \int_{v=0}^{v=v_{\text{total}}} f(v) dv, \quad (4)$$

where v is the volume of treated water (L); $f(v)$ is the function of v , determined by the relationship between dissolved LDHs and v . The percentage of total dissolved LDHs can be calculated, as follows:

$$\text{The percentage of total dissolved LDHs} = \frac{\text{The total dissolved LDHs}}{4\text{g} \times 95\%} \times 100, \quad (5)$$

3. Results and discussion

3.1 Performance of granular Ca-Al- CO_3 LDHs.

The results of Ca^{2+} and Al^{3+} dissolution are shown in Figure S2. For extrusion granules, Ca^{2+} dissolution was in the range of 30-55 mg/L, with relatively higher leaching from a higher LDHs content. Al^{3+} dissolution was in the range of 4.3-14.3 mg/L. The pH of the solution increased to ~ 11.2 . Al^{3+} concentrations dropped to 0.6-1.7 mg/L after the pH of the solution acidified to 7 at which the Al^{3+} is mainly precipitated to form $\text{Al}(\text{OH})_3$ (Wei et al. 2020). Based on the measured concentrations of Ca^{2+} at pH 7, the dissolution of LDHs of extrusion granules ranged from 14% to 20% (Figure 4A). For dropping beads, Ca^{2+} leaching was in the range of 73-116 mg/L which probably originated from CaCl_2 solution, because the Ca^{2+} concentration leached from the dropping beads with 0% of LDHs in the first run and second run was 114 mg/L and 1.5 mg/L, respectively. Similar to extrusion granules, Al^{3+} leaching from dropping beads was in the range of 4.6-11.5 mg/L and dropped to 0.5-1.6 mg/L after the pH of the solution acidified to 7. Based on the measured concentrations of Ca^{2+} at pH 7 in the second run, the dissolution of LDHs of dropping bead ranged from 3% to 11% (Figure 4A). The pH increased to 8-10.8, which confirmed the varying degrees of dissolution of LDHs. For both extrusion granules and dropping beads, less LDHs were dissolved compared with

powdered LDH (~78% dissolved at pH 7) (Wei et al. 2020).

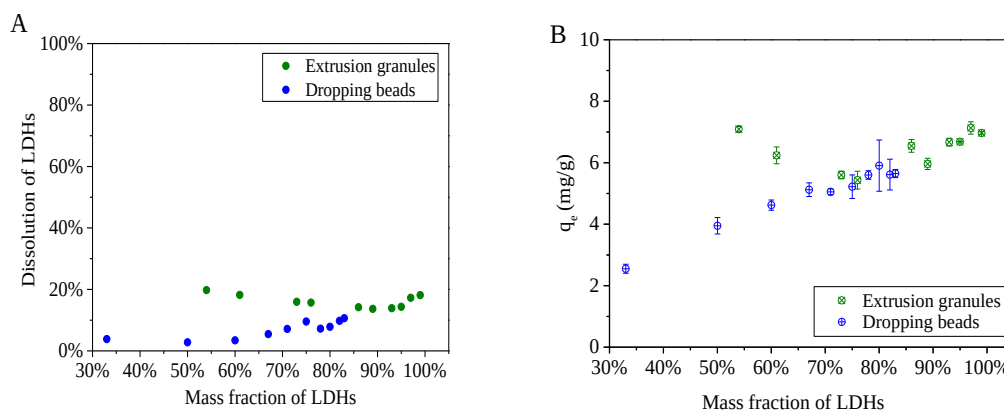


Figure 4. Dissolution (A) and F^- removal capacity (B) (Granules dose=1 g/L; initial F^- concentration=10 mg/L; pH=7; temperature=22±2°C) of granular Ca-Al-CO₃ LDHs at varying LDHs mass fractions.

Figure 4B shows the F^- removal capacity of extrusion granules and dropping beads at varying Ca-Al-CO₃ LDHs mass fraction. Generally speaking, the granules with a higher LDHs dissolution (cf. Figure 4A) and a higher LDHs content had a higher F^- removal capacity. Compared with powder Ca-Al-CO₃ LDHs (8.3 mg/g), granular LDHs had a relatively lower (2.5-7.1 mg/g) but still promising F^- removal capacity (30%-86% of powdered LDHs). For extrusion granules, high content of LDHs were obtained (up to 99%) and the F^- removal capacity ranged from 5.4 mg/g to 7.1 mg/g. For dropping beads, high content of LDHs could not be obtained and the F^- removal capacity ranged from 2.5 mg/g to 5.9 mg/g. However, the extrusion granules with >95% of LDHs were easily dispersed after soaking, making them less attractive for application. Also, the dropping beads with a higher content of LDH (>78%) were found to cause clogging of the injector during the synthesis process, making their production process less favourable. Thus the extrusion granules with 95% of LDHs and the dropping beads with 78% of LDHs were selected for further experiments.

3.2 Effect of pH

Figure 5 shows the results of batch experiments of the pH effect (HCl and CO₂ acidification) on F^- removal by extrusion granules (95% LDHs) and dropping beads (78% LDHs). In general, the LDHs granules showed a higher F^- removal efficiency at lower pH (<8) and they performed slightly better when the pH was adjusted using HCl than CO₂, which is

consistent with previous results on powdered LDHs (Wei et al, 2020). A higher F^- removal capacity at a lower pH was observed in previous results on powdered LDHs (Wei et al., 2019) and other materials such as alumina (Viswanathan and Meenakshi, 2010), hydroxyapatite (Jiménez-Reyes and Solache-Ríos, 2010) and $KMnO_4$ -modified activated carbon (Daifullah et al., 2007) due to their positively charged surfaces.

At pH 7, apart from the extrusion granules with HCl acidification, the percentage of F^- removal by dropping beads and extrusion granules ranged from 73%-76%, which is slightly lower than that by powdered LDHs (85%-90%) at the same dosage (1 g/L) and the same initial F^- concentration (10 mg/L) (Wei et al, 2020). It should be noted that the content of LDHs in extrusion granules and dropping beads are 95% and 78%, respectively. Therefore, the results indicate a competitive F^- removal capacity of granulated LDHs.

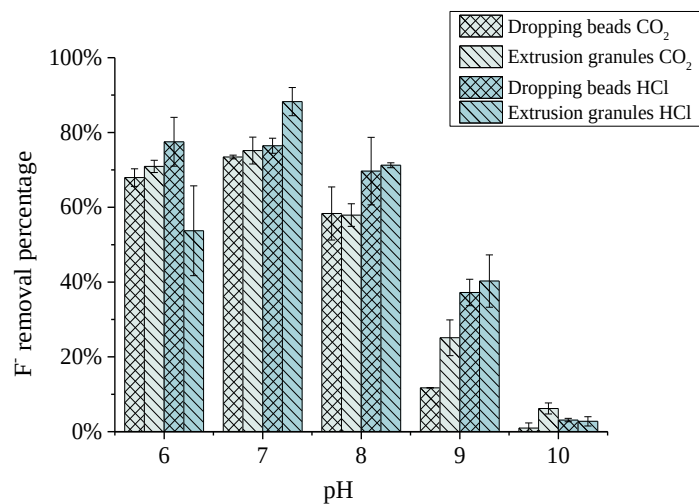


Figure 5. pH effect on F^- removal by dropping beads and extrusion granules.

(Granule dose=1 g/L; F^- =10mg/L; Temperature=20±2°C; Time=30+1 h)

3.3 Mass balance in consecutive runs in batch experiments

To better understand dissolution and for the further application of the granules, the mass balance of the extrusion granules (95% LDHs) in consecutive runs was investigated. The results on F^- removal capacity (q_e) and weight loss of the granules are shown in Figure 6A. The experimental data of q_e was 7.31 mg/g, 6.96 mg/g and 5.04 mg/g in the first, second and third run, respectively. After the first, second and third runs, the weight of the granules dropped from 1g to 0.76g (24% weight loss), 0.58g (24% weight loss) and 0.47g (19% weight loss), respectively. The corresponding calculated value of q_e in the second and third

experiments is 5.56 mg/g and 4.22 mg/g, respectively, which are lower than the experimental data.

After the granules were soaked for 30 h, the pH of the F⁻-containing solution rose to 11.4, subsequently the solution was acidified to pH 7 to simulate post-acidification (cf. section 3.2). Figure 6B shows the Ca²⁺ and Al³⁺ dissolution from extrusion granules during the experiments at pH 7. A relatively higher Ca²⁺ dissolution (~50mg/L) occurred in the first two runs and Ca²⁺ dissolution was about 25 mg/L in the third run. Al³⁺ dissolution ranged from 9.9-16.2 mg/L at pH 11.4, but it reduced to <2 mg/L at pH 7. The Al³⁺ dissolution at pH 11.4 in this experiment is higher than that in Figure S2(A) (~5.1 mg/L for the granule with 95% LDHs). One reason could be the presence of F⁻ in these experiments, because Zhang et.al found that the solubility of Al can be increased with the addition of F⁻ (Zhang et al., 2017). The higher pH could be due to the exchange between F⁻ and OH⁻ (Kim et al., 2013). Based on its formula Ca₄Al₂(OH)₁₂CO₃·nH₂O (n=4-5) and the measured concentrations of Ca²⁺ and Al³⁺ approximately 20% of Ca-Al-CO₃ LDHs was dissolved during the first two runs. This result explains the weight loss of the granules and indicates the granular LDHs are more stable than powder LDHs, which dissolved completely at near-neutral pH (Wei et.al, 2020).

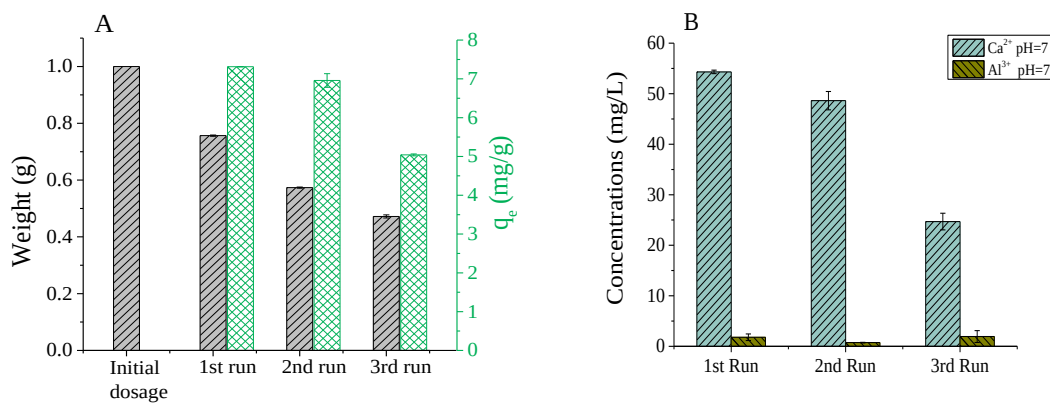


Figure 6. Mass balance, q_e (A) (Granule dose=1 g/L; F⁻=10mg/L; pH=7; T=20±2°C; Time=30+1 h) and cations dissolution (B) of extrusion granule (95% LDHs) after 3 runs.

3.4 Column study with post acidification and microfiltration

After column passage, the pH of the water increased from 7 to 11.3, which is in agreement with the batch experiments. Figure 7 shows the concentrations of F⁻ from the outlet of the column with/without subsequent CO₂ post-acidification and microfiltration. At the given conditions (C₀=5 mgF⁻/L, flow=0.5 mL/min), the F⁻ concentration in the outlet of the column increased quickly from 2.6 mg/L to 4.5 mg/L in 12h (0.36 L) then slowly to ~4.8

mg/L in 132h (3.96 L). After CO₂ acidification (back to pH=7), the F⁻ was reduced to below the WHO guideline (1.5 mg/L). These results show that Ca-Al-CO₃ LDHs granules combined with post-acidification are a promising approach for F⁻ removal .

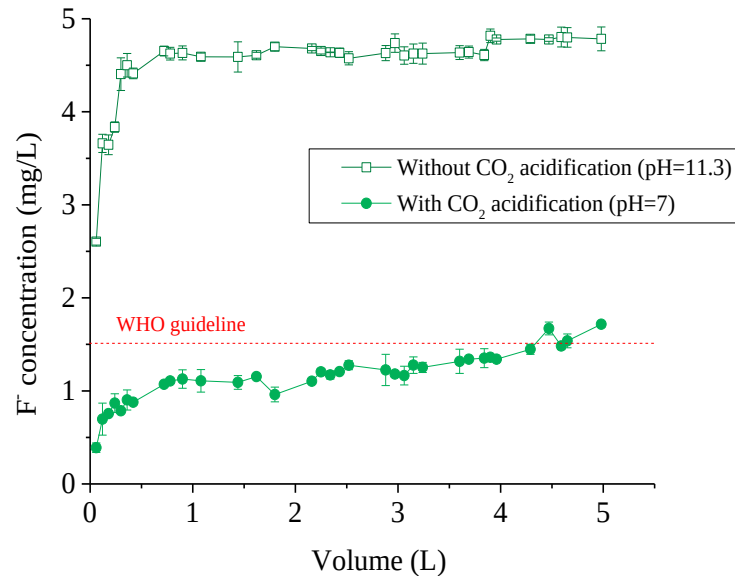


Figure 7. Concentrations of F⁻ from the effluent with/without CO₂ acidification and microfiltration. (C₀=5mgF⁻/L, influent pH≈7, Flow=0.5mL/min)

Figure 8 shows the concentrations of Ca²⁺ (A) and Al³⁺ (B) from the effluent with CO₂ acidification in the volume of treated water corresponding to different time intervals. Before CO₂ acidification, Ca²⁺ concentrations fluctuated in the range of 26.5–40.8 mg/L within 72 h (2160 mL) then suddenly rose to 74.5 mg/L and slowly decreased to 53.5 mg/L with a treated water volume of 4980 mL (Figure S3). The lower Ca²⁺ concentrations at 0–72 h (0–2160 mL) can be explained by the formation of CaCO₃ supported by PHREEQC calculation (supplementary information Figure S4). After CO₂ acidification (pH=7), Ca²⁺ concentrations continuously dropped from 82.6mg/L to 51.6mg/L. For Al³⁺, however, a single trend decreasing gradually from 25.4mg/L to 12.1mg/L was observed at pH 11.3 (Figure S3). Similar to batch experiments, Al³⁺ reduced to below 2 mg/L after CO₂ acidification (pH=7) due to precipitation. The results confirm the finding in our previous paper that apart from adsorption, re-precipitated upon partial LDHs dissolution is a key removal mechanism for F⁻ (Wei et.al, 2020).

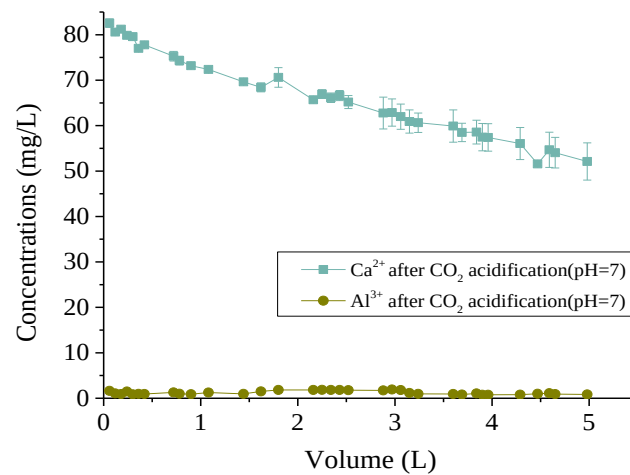


Figure 8. Concentrations of Ca^{2+} and Al^{3+} from the packed LDH bed effluent after CO_2 post-acidification. ($C_0=5\text{mgF}^-/\text{L}$, influent $\text{pH}\approx 7$, Flow= $0.5\text{mL}/\text{min}$)

Figure 9 (the left y-axis) shows the dissolved Ca-Al- CO_3 LDHs in the effluent based on the concentrations of Ca^{2+} at pH 7. The concentration of the dissolved Ca-Al- CO_3 LDHs gradually decreased as the volume (time) of treated water increased. A strongly significant negative linear correlation was found between the concentrations of dissolved Ca-Al- CO_3 LDHs and the volume of treated water ($p=0.01$, $r=0.99$). The calculated total dissolved Ca-Al- CO_3 LDHs (1.13 g) plus the remaining granular LDHs (2.72 g) is equal to 3.85 g, which is slightly lower than the amount filled in the column (4 g) indicating a weight loss during the experiment. After 166 h of operation, the cumulative dissolution of LDHs reached $\sim 30\%$ (the right y-axis of Figure 9), indicating that the LDHs granules were dissolving at a stable and slow speed.

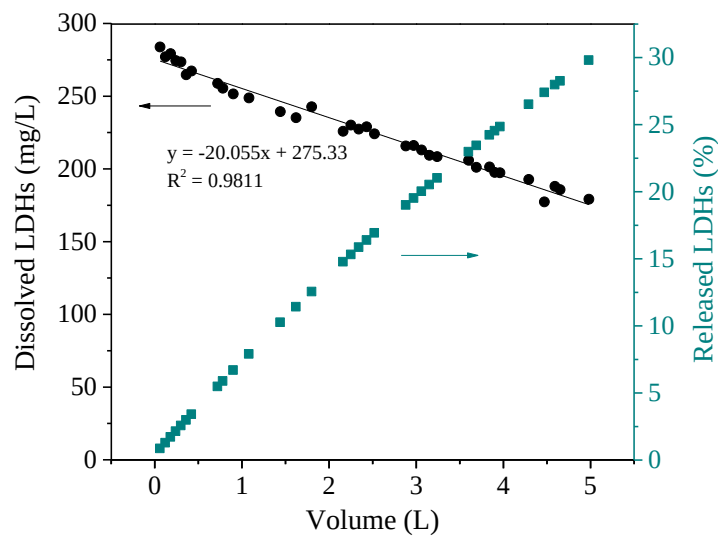


Figure 9. The dissolved LDHs (mg/L) in the effluent (the left y-axis) and the percentage of the total dissolved LDHs in the column (the right y-axis).

3.5 XRD characterization

XRD patterns of powder Ca-Al-CO_3 LDHs and the extrusion granules before and after the experiments are given in Figure 10. Compared with the powder Ca-Al-CO_3 LDHs, sharp and symmetric characteristic peaks (003 and 006) of hydrotalcite-like compounds at lower 2θ values (Cavani et al., 1991) are shown in the unused extrusion granules. A stronger signal of characteristic peaks (003 and 006) can be observed in the samples with a higher content of LDHs (Figure S5). The two characteristic peaks (003 and 006) became weaker in the granules after the experiment, which indicates the partial dissolution of the granules confirming the result of weight loss. The new characteristic peaks of CaCO_3 indicate the formation of CaCO_3 .

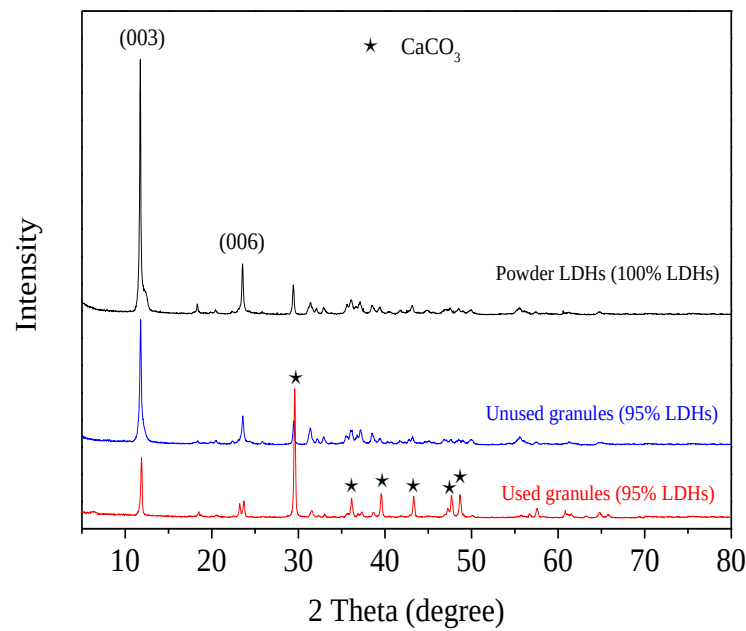


Figure 10. XRD patterns of the powder LDHs and unused/used granules (95% LDHs).

4. Conclusion

This study investigated the combination of granular Ca-Al- CO_3 LDHs packed beds with CO_2 -based post acidification and microfiltrations. This allows for sequential dissolution and precipitation of LDH-sourced calcium (Ca^{2+}) and aluminum (Al^{3+}). We found that F^- removal was effective with CO_2 post-acidification from 5 mg F^-/L to below the WHO standard of 1.5 mg/L. F^- removal capacity was found to be exceeding 30.46 mgF/gLDHs and 15.06 mgF/gLDHs, for batch and column mode, respectively. The column study demonstrated a slow and stable LDHs dissolution rate of 0.23g/L, leading to continuous and efficient F^- removal. Solids characterization by XRD confirmed precipitation of dissolved granular LDHs as particulates (CaCO_3 and hydrated Al oxides).

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Chapter 6

Conclusions and recommendations

1. Conclusions

1.1 F⁻ affinity of Ca-based materials

In this thesis, a study on F⁻ removal by mineral-based materials at environmentally-relevant concentrations was conducted, including softening pellets, geopolymers, layered double hydroxides (LDHs) and struvite. Ca-based materials including Ca-Al-CO₃ LDHs, slag-based geopolymer, and softening pellets showed the strongest affinity for F⁻. But this does not mean that the higher the content of Ca, the higher F⁻ removal capacity. The F⁻ removal capacity was also related to other factors, such as the structure, BET surface area, and Al content of the materials. While the softening pellets had the highest Ca-content (96-97%; XRF), their dense structure and consequent low BET surface area (2-3 m²/g), resulted in poorer performance than the Ca-based LDHs and slag-based geopolymers. Ca-based LDHs showed the strongest affinity for F⁻ since Ca-based LDHs had the highest Al-content (28.5%; XRF) and a relatively higher BET surface area (7.6 m²/g) than slag-based geopolymers and softening pellets.

The main mechanism of F⁻ uptake on Ca-based materials was found to be sorption at low initial F⁻ concentrations (<10 mg/L), whereas precipitation as CaF₂ is proposed to play a major role at higher initial F⁻ concentrations (>20 mg/L). This proposed mechanism was supported by hydrochemical simulations (using PHREEQC software) in this study. Similar to the present study, Turner et al. conducted F⁻ (3-2100mg/L) removal studies using crushed limestone (99% pure calcite that is CaCO₃) with the help of surface-sensitive techniques, such as atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) as well as potential measurements (Turner et al., 2005). They confirmed that a combination of surface adsorption and precipitation reactions removed F⁻ from aqueous systems and that the degree of removal depended on calcite surface area.

1.2 The dominant role of pH

Among the factors impacting F⁻ removal, including initial F⁻ concentration, adsorbent dose, pH, temperature and co-existing ions, pH played a dominant role on F⁻ removal by Ca-Al-CO₃ LDHs. It was observed that better F⁻ removal occurs at pH 6-8 compared to ≥pH 9, with the inherent problem of Ca-Al-CO₃ LDHs to react caustic upon addition to water (i.e., pH_{pzc}, pH of point of zero charge 12-13), resulting in reduced defluoridation (~5%, pH=11.5,

initial F^- = 10 mg/L). With the dose of 0.1-2 g/L, Ca-Al- CO_3 LDHs increased the pH of the solution (from approximately 6.5) to 10.8-11.5. Consequently, acidification is a pre-requisite for F^- removal with Ca-Al- CO_3 LDHs.

Some 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) also reached better F^- removals at lower pHs. One explanation is that, at pH below pH_{pzc} , the surface of adsorbents was positively charged with the decrease of pH and the net positive charge is favorable for F^- adsorption (Das et al., 2003; Wu et al., 2015). This is due to the fact that hydroxyl groups on the surface ($\equiv M$) of LDHs were protonated at low pH and the sorption was dominated by the electrostatic interaction (Wu et al., 2017). 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).

In our experiments at pH 6-8, Ca-Al- CO_3 LDHs showed affinity for F^- from synthetic groundwater in the environmentally-relevant lower concentration ranges (2-12 mg/L) to below the WHO guideline (1.5 mg/L). It was found that the addition of HCl and CO_2 to LDHs suspensions led to damages in the LDHs structure, leading to F^- adsorption or complexation onto/into various rehydrated mixed metal oxides. The combination of granular Ca-Al- CO_3 LDHs packed beds with CO_2 -based post acidification and microfiltration allows for sequential dissolution and precipitation of LDH-sourced calcium (Ca^{2+}) and aluminum (Al^{3+}), removed by a microfiltration step. The column study demonstrated a slow and stable LDHs dissolution leading to continuous and efficient F^- removal with CO_2 post-acidification from 5 mg F^- /L to below the WHO standard of 1.5 mg/L.

1.3 The mechanism of dissolution-precipitation

The main mechanism of F^- removal by powdered Ca-Al- CO_3 LDHs was proposed as F^- adsorption or complexation onto/into various rehydrated mixed metal oxides which re-precipitate upon partial LDHs dissolution when acidifying. The mechanism of dissolution-precipitation can be better understood in the study on F^- removal by the combination of granular Ca-Al- CO_3 LDHs packed beds with CO_2 -based post acidification and microfiltration.

The dissolution of Ca-Al- CO_3 LDHs was reflected in the increase in pH of the solution and the leaching of Ca^{2+} after LDHs dosing. Based on the formula of $Ca_4Al_2(OH)_{12}CO_3 \cdot nH_2O$ ($n=4-5$), the investigated Ca-Al- CO_3 LDHs is rich in OH and Ca. The released OH^- explains

why the pH of the solution increased and also indicates the dissolution of Ca-Al-CO₃ LDHs. Based on its formula and the measured concentrations of Ca²⁺, approximately 24% of Ca-Al-CO₃ LDHs (initial concentrations = 1 g/L) was dissolved with no pH control and over 94% (273 mg/L) and 83% (241 mg/L) dissolved at pH 6 for HCl and CO₂ acidification, respectively. After granulation, the dissolution of LDHs of extrusion granules and dropping beads ranged from 14% to 20% and from 3% to 11%, respectively. pH adjusting by addition of HCl and CO₂ to LDHs suspensions led to damages in the LDHs structure, demonstrated by SEM, EDX, XRD, and FTIR. A certain dissolution (~20%) of LDHs is advantageous for F⁻ removal but a high dissolution (>30%) leads to a lot of loss of LDHs, and a low dissolution (<15%) cannot reach the goal of F⁻ removal.

After acidification, the dissolved Ca²⁺, Al³⁺, OH⁻ and CO₃²⁻ creates excellent conditions for F⁻ removal. On the one hand, F⁻ can be adsorbed onto the precipitate of CaCO₃ (Budyanto et al., 2015; Turner et al., 2005). On the other hand, F⁻ can be removed by adsorption or complexation onto/into various rehydrated Al oxides which re-precipitated when acidifying because Al-containing precipitates were formed from the previously dissolved LDHs, then F⁻ be removed from solution onto such precipitates (He et al., 2015; Lu et al., 2000a). 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 boemite (γ -AlOOH) to amorphous Al species with decreasing pH from 11 to 6 (Du et al., 2009). PHREEQC modelling showed that the various Al-containing species such as Al(OH)₂⁺, AlF²⁺, AlF₂⁺, Al(OH)₄⁻, etc. were present under the tested conditions. Solids characterization by XRD confirmed precipitation of dissolved granular LDHs as particulates (CaCO₃ and hydrated Al oxides). In addition, it was observed that the granules with a higher LDHs dissolution and a higher LDHs content had a higher F⁻ removal capacity.

2. General outlook and recommendations

This thesis showed an efficient F⁻ removal from synthetic groundwater in the environmentally-relevant lower concentration ranges (2-12 mg/L) to below the WHO guideline (<1.5 mg/L). The residuals of anions (Cl⁻) and cations (Ca²⁺ and Al³⁺) are acceptable for drinking water consumption under reasonable pH adjustment acid and proper treatment process conditions. The combination of granular Ca-Al-CO₃ LDHs packed beds with CO₂-based post acidification and microfiltration will result in cost savings and lower anions

(Cl^-) and cations (Ca^{2+}) residuals compared to HCl acidification. In practice, the Ca-Al- CO_3 LDHs granules need to be frequently added due to continuous dissolution. The use of local materials in synthetic LDHs will reduce the costs of transportation and operation.

Even though the research covered many aspects concerning F^- removal, including the development of F^- removal material, the modification of the materials, granulation and the column study, there are still aspects that were either not covered or require further understanding as indicated below, and recommendations for future research:

- A future study exploring Ca-based materials to remove F^- by CaF_2 precipitation at low F^- concentrations is recommended, for example, by adding a process (e.g. electrocoagulation) to increase the F^- concentration, to start the precipitation and better understand the mechanism.
- Further modification studies on softening pellets should be considered in the future to enhance the F^- removal capacity (e.g. increase the surface area). Softening pellets generally have a high Ca-content, but their dense structure and consequent low BET surface area (2-3 m^2/g), resulted in poorer F^- removal performance.
- Future research is also recommended to focus on improving the pH adaptability of Ca-Al- CO_3 LDHs, considering that defluoridation by Ca-Al- CO_3 LDHs is highly pH sensitive, with better removals at pH 6-8 compared to $\geq \text{pH } 9$ and the addition of HCl and CO_2 to LDHs suspensions led to changes to the LDHs structure. Additional research such as transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) is recommended to further examine this F^- removal mechanism.
- From a practical perspective, it would be recommended to investigate the optimization of combining CO_2 post-acidification, microfiltration and Ca-Al- CO_3 LDHs and other $\text{Ca}^{2+}/\text{Al}^{3+}$ -based minerals under field conditions. Particularly, the reusability of Ca-Al- CO_3 LDHs and a lower Al^{3+} residue in real groundwater applications should be further examined.

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Appendix A - Supplementary material Chapter 3

1. Adsorption isotherm:

Adsorption isotherms describe the equilibrium relationships between adsorbent and adsorbate, and thus are critical for the design of the adsorption systems (El-Khaiary, 2008). The two most widely-used isotherms models, Langmuir model (Eq.(1)) (Langmuir, 1917) and Freundlich model (Eq.(2)) (Freundlich, 1906) were applied to interpret the adsorption isotherm data. The use of the Langmuir isotherm suggests that monolayer adsorption occurs at specific homogeneous sites (Kundu and Gupta, 2006). Freundlich isotherm assumes that the stronger binding sites of the sorbent are occupied first and that the binding strength decreases with the increasing degree of site occupation (Vijayaraghavan et al., 2006). Freundlich isotherm is not restricted to the formation of monolayer but can be applied to multilayer adsorption over the heterogeneous surface (Foo and Hameed, 2010).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

where K_L is the Langmuir constant related to the loading capacity and the free energy of adsorption; q_m is the theoretical maximum monolayer sorption capacity (mg/g); K_F and n are the Freundlich constants.

2. Kinetic studies:

Four most commonly used models, Pseudo-first-order model (Eq. 3), Pseudo-second-order model (Eq. 4), Elovich equation model (Eq. 5), and Intraparticle diffusion model (Eq. 6) were fitted to the kinetic experimental data (Blanchard et al., 1984; Ho and McKay, 1998; Ho et al., 1996; Lagergren, 1898; McLintock, 1967; Weber and Smith, 1987).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (5)$$

$$q_t = k_i t^{0.5} + C \quad (6)$$

where k_1 and k_2 are the pseudo-first and pseudo-second order kinetic rate constant (min^{-1}), respectively; α and β are the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and the desorption constant (g mg^{-1}) respectively; where k_i is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{0.5}$), C is the intercept which is related to boundary layer thickness. The parameters of the four models were determined by plotting graphs of $\ln(q_e - q_t)$ versus t , t/q_t versus t , q_t versus $\ln t$, q_t versus $t^{0.5}$, respectively.

3. PHREEQC calculation

PHREEQC is a geochemical model that can be applied in speciation and saturation-index calculations, batch-reaction, one-dimensional reactive-transport, and inverse modeling (Parkhurst and Appelo, 2013a). F^- solution was defined by using the experimental major-ion data. In the PHREEQC input file, initial concentrations of F^- and Ca^{2+} were fixed to the desired values. Detailed descriptions of simulation and input files can be found in example 1 from Parkhurst and Appelo (Parkhurst and Appelo, 2013a).

4. Cost estimate calculation:

The analysis of cost estimate was carried out using the measured F^- uptake capacity of Ca-Al- CO_3 LDHs (6.7 mg/g), and the price of $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot n\text{H}_2\text{O}$ ($n=4-5$) LDH (ACTILOX[®] CAHC) (€3-4/kg) obtained from Nabaltec (Germany). According to our experimental data, 1 kg of untreated Ca-Al- CO_3 LDHs with a F^- uptake capacity of 6.7 mg/g can be used to treat about 788 L of F^- contaminated water and reduce the F^- concentration from 10mg/L to below the WHO guideline. Ca-Al LDHs can be synthesized using the co-precipitation method with CaCl_2 and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Sun et al., 2017). The source of calcium and aluminum can be other calcium aluminum salts (e.g. CaCO_3 , $\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$) (François et al., 1998) which are readily available in developing countries. Ca-Al LDHs can also be obtained from waste produced by the bauxite refinery industry (red mud) (Palmer et al., 2009). Thus synthesis of a kilogram of Ca-Al- CO_3 LDHs costs could be lower than €3-4. For acidification, about 1mL HCl (1M) was added to adjust the pH of the solution (0.1L) from 11.5 to 8 with the Ca-Al- CO_3 LDHs dose of 1g/L. 1 L of HCl (1M) (€20.7/L, VWR) can be used to treat 100 L water. The cost of the acid might be an obstacle for application. But if 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.

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Table S1 Isotherm constants for F⁻ uptake on Ca-Al-CO₃ LDH and its modified products.

Adsorbents	Langmuir model			Freundlich model		
	$q_e = (q_m K_L C_e) / (1 + K_L C_e)$			$q_e = K_F C_e^{1/n}$		
	q_m	K_L	R_1^2	K_F	n	R_2^2
	(mg/g)	(L/mg)		(mg/g)(L/mg) ^{1/n}		
Ca-Al-CO ₃ LDHs	25.88	0.23	0.999	4.81	1.30	0.995
Calcined Ca-Al-CO ₃ LDHs	59.38	0.11	0.997	5.74	1.11	0.996
Microwave treated Ca-Al-CO ₃ LDHs	34.13	0.18	0.985	5.19	1.21	0.984

Table S2 Kinetic models and their parameters.

Adsorbents	$q_{e,exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order			Elovich			Intraparticle diffusion					
		$ln(q_e-q_t)=ln q_e-k_1t$			$t/q_t=1/(k_2q_e^2)+t/q_e$			$q_t=1/\beta ln (\alpha\beta)+1/\beta lnt$			$q_t=k_i t^{0.5}+C$					
		$q_{e,cal}$	k_1	R^2	$q_{e,cal}$	k_2	R^2	α	β	R^2	k_{i1}	R_1^2	k_{i2}	R_2^2	k_{i3}	R_3^2
		(mg/g)	(min ⁻¹)		(mg/g)	(min ⁻¹)										
Ca-Al-CO ₃ LDHs	6.31	1.8	0.017	0.956	6.38	0.042	0.992	6045	2.404	0.936	0.469	0.887	0.176	0.97	0.064	0.898
Calcined Ca-Al-CO ₃ LDHs	7.09	2.17	0.019	0.957	7.18	0.04	0.998	1036	1.808	0.984	0.717	0.91	0.185	0.996	0.069	0.918
Microwave treated Ca-Al-CO ₃ LDHs	7.16	2.12	0.018	0.812	7.22	0.043	0.999	661	1.715	0.971	0.641	0.817	0.247	0.854	0.067	0.777

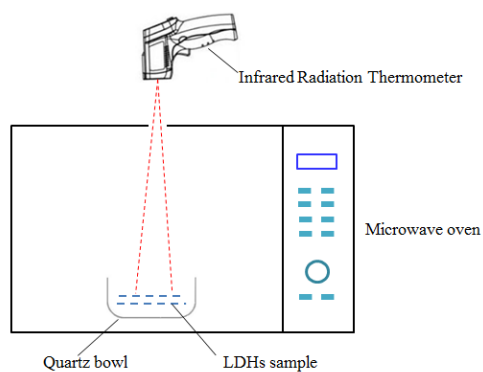


Fig. S1. Schematics of microwave irradiation.

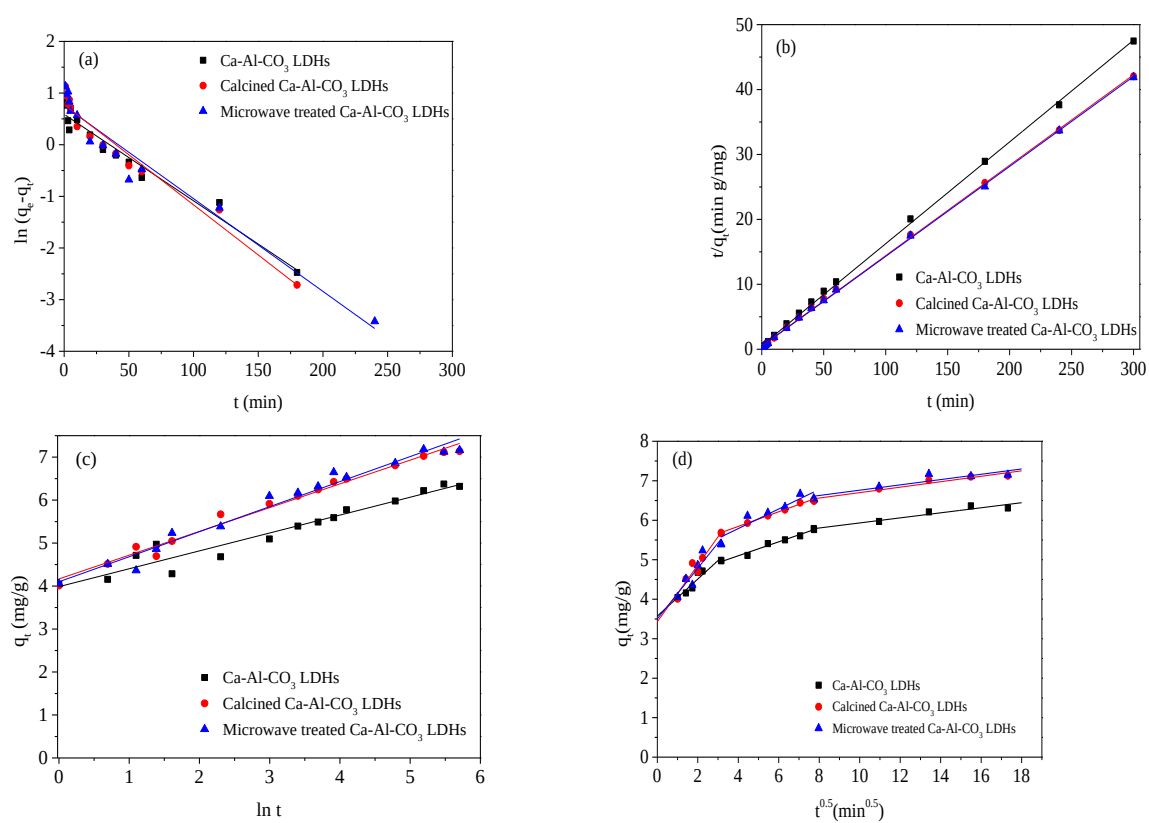


Fig. S2. First-order kinetics model (a), Pseudo-second-order kinetics model (b), Elovich equation model (c) and Intraparticle diffusion model (d) fitting of the adsorption kinetics.

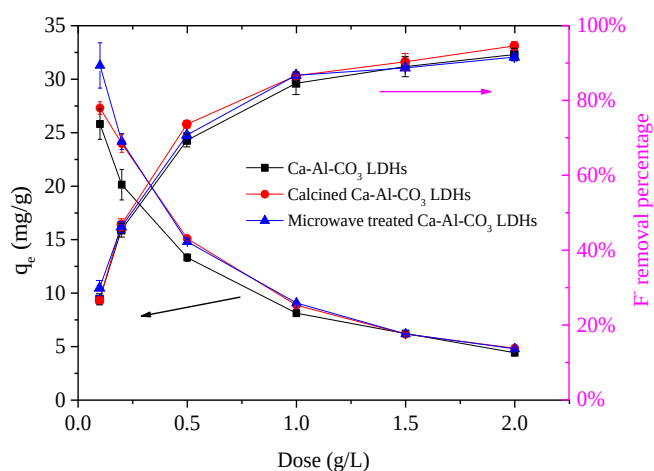


Fig. S3. Effect of adsorbent dose on the F⁻ removal by Ca-Al-CO₃ LDH and its modified products.

(Initial F⁻=10 mg/L; pH=8; adsorbent dose=0.1-2g/L; T=25±1°C)

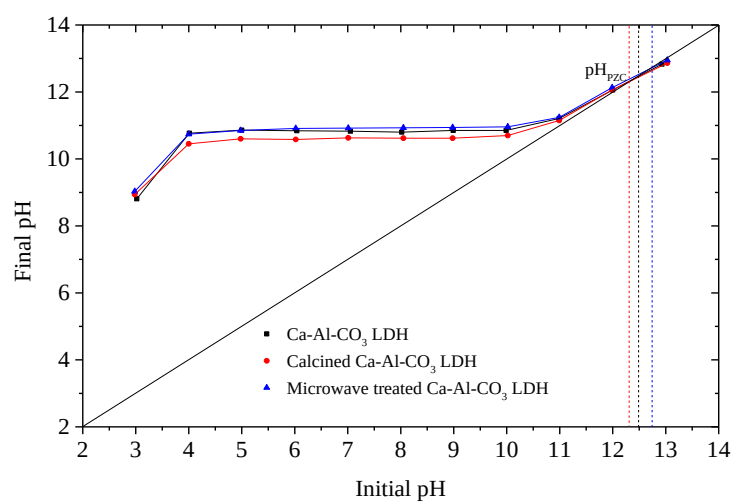


Fig. S4. The pH of the point of zero charge (pH_{pzc}) of Ca-Al-CO₃ LDHs and its modified products.

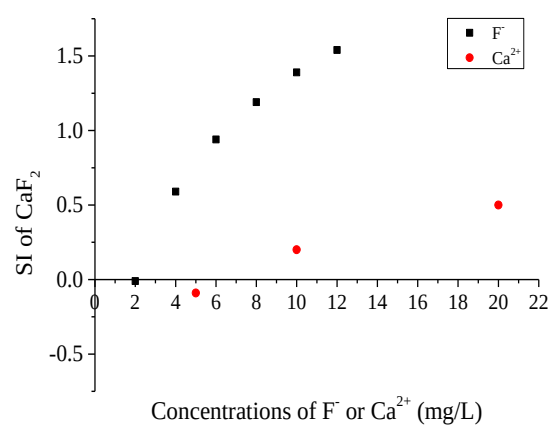


Fig. S5. The effect of F^- and Ca^{2+} concentrations on the saturation-index value of CaF_2 .

Appendix B - Supplementary material Chapter 4

1. Effect of adsorbent dose

The results of the effect of Ca-Al-CO₃ LDHs dose are presented in Figure S1. A similar result can be observed between HCl and CO₂ that the q_e increased when the LDHs dose increased from 0.1 g/L to 0.2 g/L but decreased when the LDHs dose increased from 0.2 g/L to 2 g/L. The highest q_e is observed at the LDHs dose of 0.2 g/L instead of 0.1 g/L. This is different from some previous studies (Kim et al., 2013; Zhang et al., 2012) and our previous study at pH 8 (Wei et al., 2019). This might be due to the negative influence of pH-adjusting acids on Ca-Al-CO₃ LDH. Although Cl⁻ does not compete with F⁻ at high LDHs dose (1 g/L), some loading sites or pores might be occupied by Cl⁻ (470 mg/L) at low LDHs dose (0.1 g/L). Another explanation could be the dissolution of Ca-Al-CO₃ LDH, which has a stronger negative effect on q_e when the LDHs dose is lower. It can be found from Figure S1 that Ca-Al-CO₃ LDHs showed a higher q_e when HCl was used as the pH-adjusting acid. And the difference is much bigger at a lower adsorbent dose (<1 g/L). This could be due to the competition between HCO₃⁻ and F⁻ because our previous study showed that a high concentration of HCO₃⁻ has a negative effect on F⁻ removal (Wei et al., 2019). The influence of competition reduced at a higher adsorbent dose (>1 g/L) due to the sufficient loading sites.

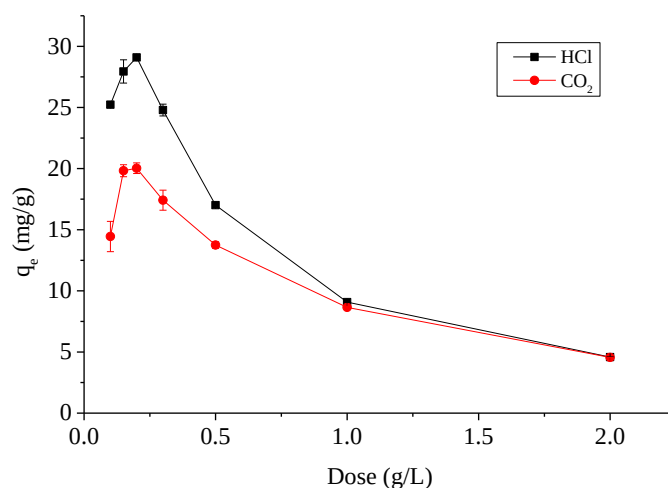


Figure S1. The effect of adsorbent dose.

(Initial F⁻=10 mg/L; pH=6; adsorbent dose=0.1-2g/L; T=22±1°C)

2. F⁻ removal equilibrium

The isotherm of F⁻ uptake by Ca-Al-CO₃ LDHs under pH 6 (acidified by HCl and CO₂)

are given in Figure S2. The isotherms under both pH conditions (acidified by HCl and CO₂) were L-type curves with a plateau (Limousin et al., 2007). As can be observed, the F⁻ removal capacity at equilibrium (q_e) increased with the increase of equilibrium F⁻ concentrations (C_e). For all initial F⁻ concentrations (2-12 mg/L), Ca-Al-CO₃ LDHs presented a higher q_e when pH was adjusted by HCl than by CO₂. This result indicates a negative effect of CO₂, which is consistent with the results of section 3.1.

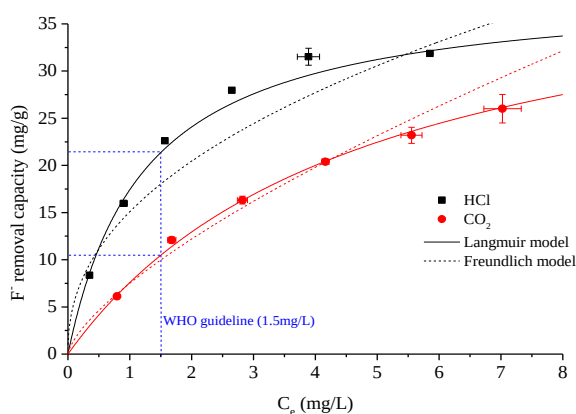


Figure S2. Isotherm of F⁻ uptake by Ca-Al-CO₃ LDHs under HCl and CO₂ pH adjustment conditions.

(Initial F⁻=2,4,6,8,10,12 mg/L; pH=6; LDHs dose=0.2 g/L; T=22±1°C)

Assuming strictly adsorptive removal processes, the equilibrium data have been fitted to the Langmuir model and Freundlich model. The fitting results are presented in Figure S2 and Table S1. All of the data can be fitted well to the Langmuir model ($R^2=0.997$). The maximum F⁻ removal capacity (q_m) of Ca-Al-CO₃ LDHs reached 44.03 mg/g and 38.92 mg/g at pH 6 adjusted by HCl and CO₂, respectively. At the equilibrium concentration of WHO guideline (1.5 mg/L), the F⁻ removal capacity of Ca-Al-CO₃ LDHs was approximately 21.4 mg/g and 10.5 mg/g at pH 6 adjusted by HCl and CO₂, respectively.

Table S1 Isotherm constants for F⁻ uptake on Ca-Al-CO₃ LDHs.

Acid	Langmuir model			Freundlich model		
	$q_e = (q_m K_L C_e) / (1 + K_L C_e)$			$q_e = K_F C_e^{1/n}$		
	q_m	K_L	R^2	K_F	n	R^2
	(mg/g)	(L/mg)		(mg/g)(L/mg) ^{1/n}		
HCl	44.03	0.208	0.997	15.087	2.280	0.957
CO ₂	38.92	0.811	0.997	7.511	1.430	0.985

3. Kinetic modeling

The kinetic experimental data of F⁻ dose before acidification (mean value) have been fitted to kinetic models including Pseudo-first-order model, Pseudo-second-order model, and Intraparticle diffusion model. The results are presented in Figure S3 and table S2. It can be observed that the experimental data both for HCl and CO₂ fitted well with the Pseudo-second-order model ($R^2 > 0.93$) (Figure S3b). The calculated F⁻ removal capacity ($q_{e,cal}$) of Ca-Al-CO₃ LDHs for HCl and CO₂ was 10.19 mg/g and 8.63 mg/g, respectively, which are close to the experimental data (9.11 and 8.88 mg/g, respectively). The results suggest that the removal process involves chemical interactions (Daifullah et al., 2007; Inyang et al., 2016). Figure 3c shows that the plots of q_t versus $t^{0.5}$ can be divided into two separate linear stages and all of the plots do not pass through the origin. The rate-limiting process is due to intraparticle diffusion if the linear plots pass through the origin (Gupta and Bhattacharyya, 2011b). Thus the rate-limiting process is not only because of intraparticle diffusion (Chang et al., 2011b). One thing needs to be noticed that data presented in Figure 3c is the mean value and there is a big standard deviation for the data points of the first 5 min when the pH was adjusted by HCl. And the intercept of this stage ($t^{0.5} < 2.24$) is less than 0, which could possibly due to intraparticle diffusion.

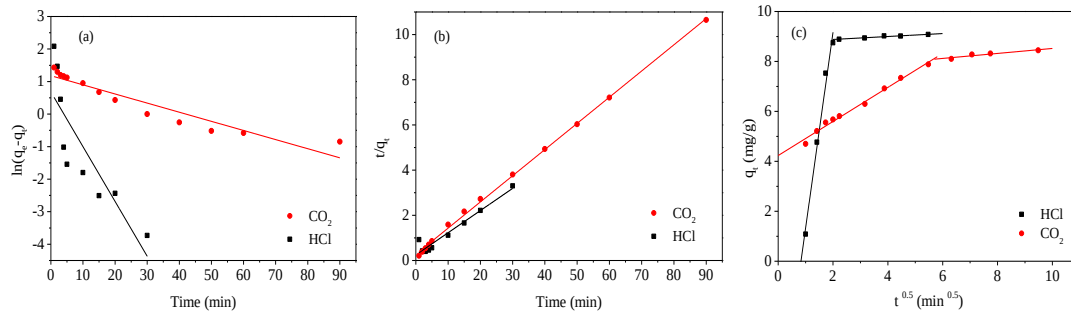


Figure S3. First-order kinetics model (a), Pseudo-second-order kinetics model (b) and Intraparticle diffusion model (c) fitting of the removal kinetics.

Table S2 Kinetic models and their parameters.

Acid	Pseudo-first-order				Pseudo-second-order			Intraparticle diffusion			
	$q_{e,exp}$	$\ln(q_e - q_t) = \ln q_e - k_1 t$			$t/q_t = 1/(k_2 * q_e^2) + t/q_e$			$q_t = k_i t^{0.5} + C$			
	(mg/g)	$q_{e,cal}$	k_1	R^2	$q_{e,cal}$	k_2	R^2	k_{i1}	R_1^2	k_{i2}	R_2^2
		(mg/g)	(min ⁻¹)		(mg/g)	(min ⁻¹)					
HCl	9.11	1.98	0.168	0.688	10.19	0.039	0.936	7.846	0.979	0.059	0.925
CO ₂	8.88	3.25	0.028	0.899	8.63	0.049	0.999	0.682	0.987	0.099	0.846

4. PHREEQC calculation

PHREEQC is a geochemical model that can be applied in speciation and saturation-index calculations, batch-reaction, one-dimensional reactive-transport, and inverse modeling (Parkhurst and Appelo, 2013b). F⁻ solution was defined by using the experimental major-ion data. Detailed descriptions of simulation and input files can be found in example 1 from Parkhurst and Appelo (Parkhurst and Appelo, 2013b).

Input files used in this paper:

TITLE Species distribution of Al-Ca-F using HCl acidification

SOLUTION 1

temp 25
 pH 11.45
 pe 4
 redox pe

```

units      mg/l
density    1
Alkalinity 1125  as Ca0.5(CO3)0.5
F          10
Na         12.105
Ca         70
Al         70
-water     1 # kg

```

END

PHASES

Fix_H+

H+ = H+

log_k 0

TITLE HCl acidification

USE solution 1

EQUILIBRIUM_PHASES 1

CO2(g) -10

Fix_H+ -6 HCl 10 #varied to -10 HCl 10

END

TITLE Species distribution of Al-Ca-F using CO2 acidification

SOLUTION 1

```

temp        25
pH          11.45
pe          4
redox       pe
units       mg/l
density     1
Alkalinity 1125  as Ca0.5(CO3)0.5
F           10
Na          12.105
Ca          70
Al          70

```

```

-water      1 # kg
END
TITLE CO2 dissolution/acidification
USE solution 1
EQUILIBRIUM_PHASES
CO2(g)  0.008  # varied to -4.6
END

```

5 Cost estimate calculation

The analysis of cost estimate was carried out using the measured F^- uptake capacity of Ca-Al- CO_3 LDHs (8.5 mg/g and 9.1 mg/g at pH 7 adjusted by HCl and CO_2 , respectively)(Figure 3A), and the price of $Ca_4Al_2(OH)_{12}CO_3 \cdot nH_2O$ ($n=4-5$) LDH (ACTILOX[®]CAHC) (€3-4/kg) obtained from Nabaltec (Germany). According to our experimental data, 1 kg of Ca-Al- CO_3 LDHs with a F^- uptake capacity of 8.5 mg/g or 9.1 mg/g can be used to treat about 1 m³ or 1.07 m³ of F^- contaminated water and reduce the F^- concentration from 10mg/L to below the WHO guideline. The cost of Ca-Al- CO_3 LDHs for 1 m³ water is €3-4 and €2.8-3.7 with acidification by HCl and CO_2 , respectively. For acidification by HCl, about 1.15mL HCl (1M) was added to adjust the pH of the solution (0.1L) from 11.5 to 7 with the Ca-Al- CO_3 LDHs dose of 1g/L. 1 L of HCl (1M, € 20.7) can be used to treat 0.087 m³ water. The cost of the acid is € 238 per m³ water. For acidification by CO_2 , about 70mL CO_2 was bubbled in 0.1L suspension with a flow of 5-10mL/min for 5-10min. 1L of CO_2 (€ 2.02 per kg = € 2.02/1000g*44g/mol/22.4L/mol = € 0.00397 per L) can be used to treat 0.0014 m³ water. The cost of CO_2 is € 2.78 per m³ water. Thus the cost of acids are much higher than Ca-Al- CO_3 LDHs. Accordingly, the chosen acidification method is the main cost driver and an LDH treatment step with CO_2 acidification invokes substantially reduced costs as compared to HCl acidification, despite the lower LDH performance under CO_2 . Besides lower costs, CO_2 outcompetes any concentrated liquid acid (e.g. HCl) in terms of practicability, since it does not involve the introduction of potentially undesired anions.

It should be noted that the bubbled CO_2 was not completely dissolved. The measured concentration of CO_3^{2-} in the 0.1L suspension is about 550mg/L that is 9.167 mmol CO_3^{2-} /L,

equals 20.5mL of CO₂ (=9.167 mmol/L*0.1L*22.4L/mol). Less than half of the bubbled CO₂ was dissolved. Thus the acidification cost will be much lower if the bubbled CO₂ can completely dissolved with a sealed container. Ca-Al LDHs can be synthesized using the co-precipitation method with CaCl₂ and AlCl₃·6H₂O (Sun et al., 2017). The source of calcium and aluminum can be other calcium aluminum salts (e.g. CaCO₃, Ca(OH)₂ and Al(OH)₃) (François et al., 1998) which are readily available in developing countries. Ca-Al LDHs can also can be obtained from waste produced by the bauxite refinery industry (red mud) (Palmer et al., 2009). Thus synthesis of a kilogram of Ca-Al-CO₃ LDHs costs could be lower than €3-4.

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Table S3 Comparison of anions concentration at pH 6 with the threshold.

Anions	Start of experiment		End of experiment		Threshold
	1g/L LDHs	0.2g/L LDHs	1g/L LDHs	0.2g/L LDHs	
Cl ⁻	456	99	449	98	N.A.
NO ₃ ⁻	835	172	829	170	50
SO ₄ ²⁻	671	147	618	135	250
PO ₄ ³⁻	795	205	238	168	0.31*
HCO ₃ ⁻	N.A.	N.A.	550	125	N.A.

N.A.: Not available

*: Total P (0.05 mgP/L) in a stream at a point where it enters a lake or reservoir (Recommended by U.S. Environmental Protection Agency).

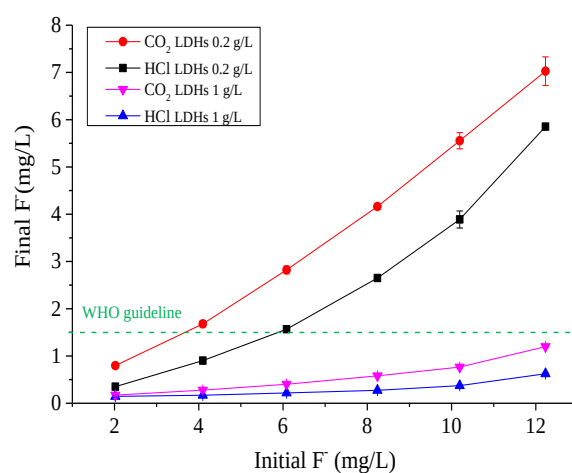


Figure S4. The effect of initial F^- concentrations on F^- removal efficiency.
(Initial F^- =2,4,6,8,10,12 mg/L; pH=6; LDHs dose=0.2 or 1 g/L; $T=22\pm 1^\circ\text{C}$)

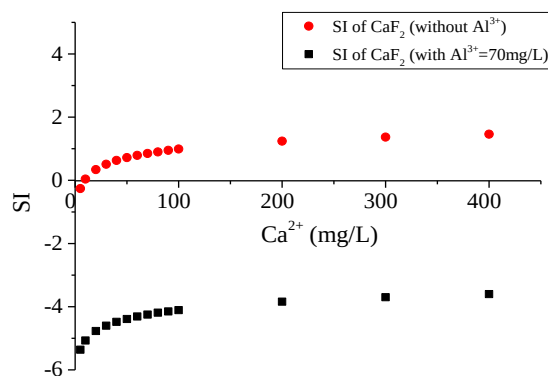


Figure S5. The SI values of CaF_2 with and without Al^{3+} .
(pH=6, F^- =10mg/L, $T=25^\circ\text{C}$)

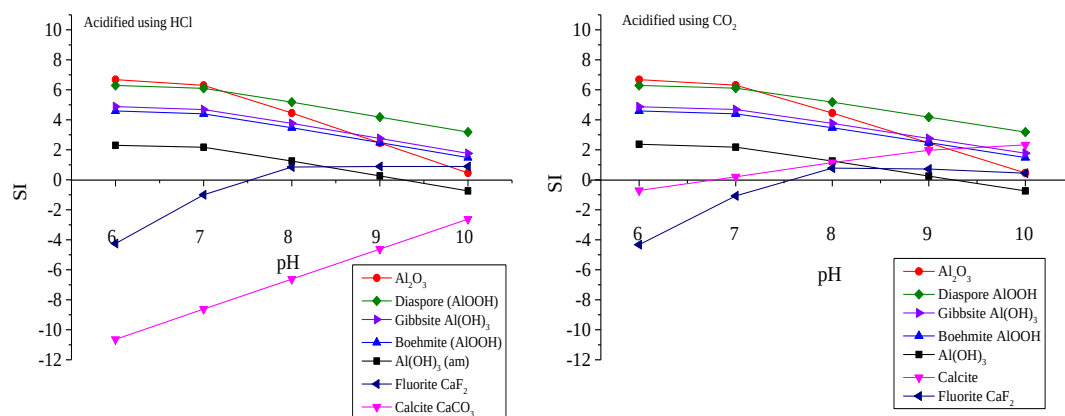


Figure S6. Effect of pH on the SI values of Al and Ca species.
(T=25°C, pH=6-10, F⁻=10mg/L, molar ratio of F⁻/Al³⁺=0.71).

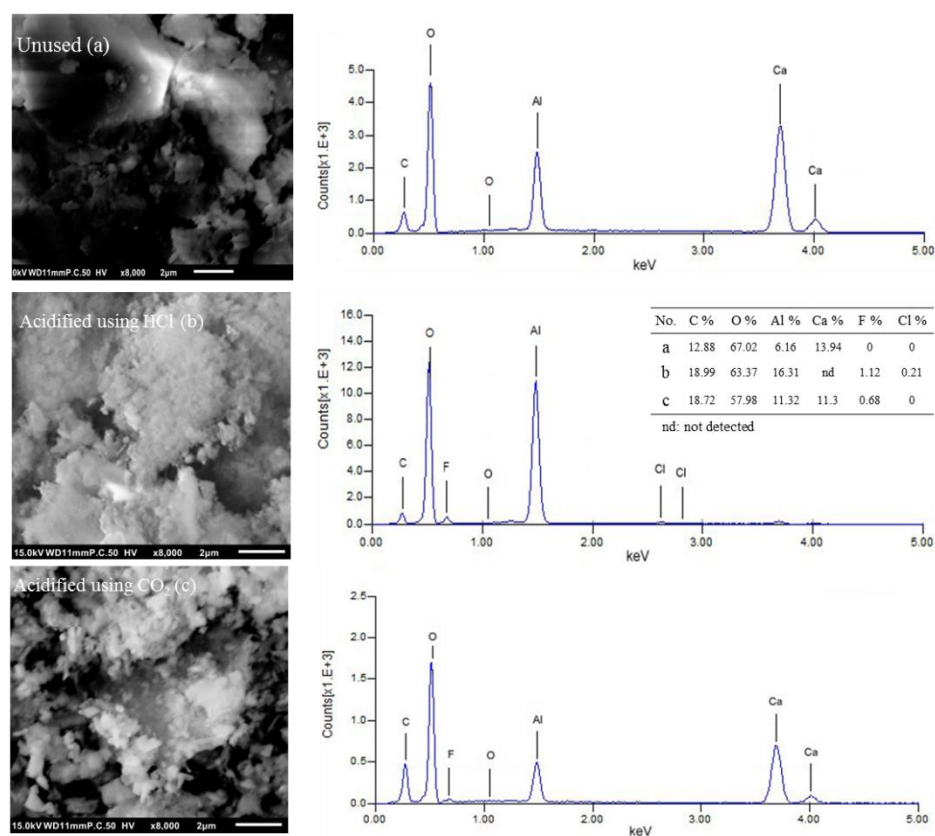


Figure S7. SEM images and corresponding EDX spectrum of Ca-Al-CO₃ LDHs before and after experiment (inset: the EDX results (atom%)).

Appendix C - Supplementary material Chapter 5

1. The equilibrium time of dissolution in the preliminary batch experiment.

1 g of extrusion granules (95% LDHs) was soaked in 1L deionized water on a shaker with a speed of 120 rpm at room temperature ($22\pm 2^\circ\text{C}$). The pH of the solution was recorded and a 3 mL sample was filtered by $0.1\ \mu\text{m}$ membrane for the analysis of Ca^{2+} concentration at different time intervals.

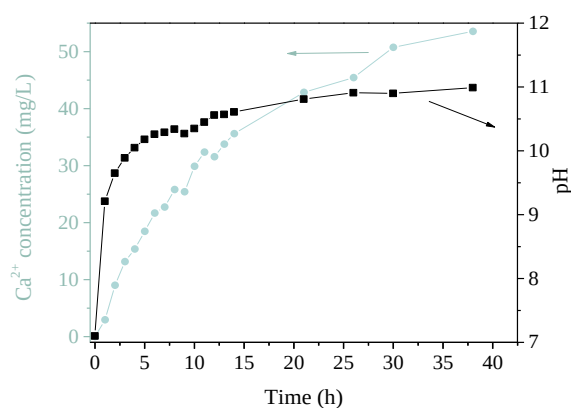


Figure S1. Ca^{2+} concentration and pH in preliminary batch experiment.

2. Ca^{2+} and Al^{3+} leaching from LDHs extrusion granules (A) dropping beads (B) at varying LDH mass fractions and two different pHs.

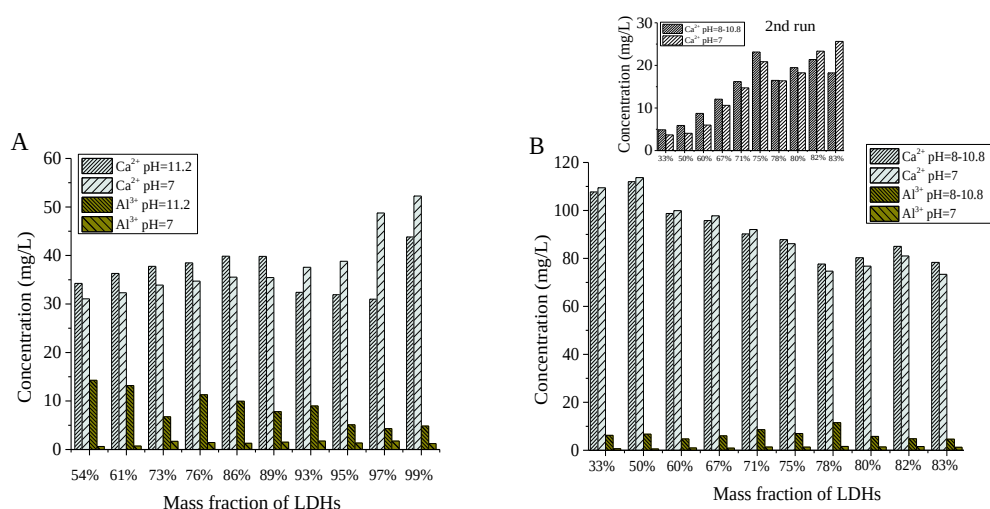


Figure S2. Ca^{2+} and Al^{3+} leaching from LDHs extrusion granules (A) dropping beads (B) at varying LDH mass fractions and two different pHs. (granular LDHs dosage=1 g/L; 100mL water; temperature= 22°C ; soaked for 30h)

3. Concentrations of Ca^{2+} and Al^{3+} from the effluent before CO_2 acidification in column study.

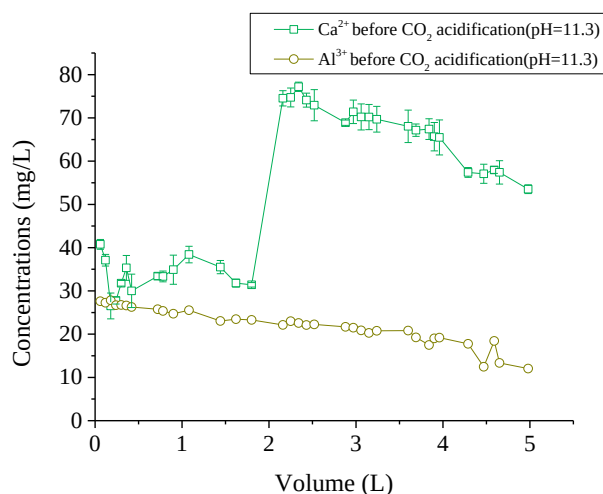


Figure S3. Ca^{2+} and Al^{3+} in the effluent before CO_2 acidification in column study.

4. PHREEQC calculation

PHREEQC is a geochemical model that can be applied in speciation and saturation-index calculations, batch-reaction, one-dimensional reactive-transport, and inverse modeling (Parkhurst and Appelo, 2013a). F^- solution was defined by using the experimental major-ion data. In the PHREEQC input file, initial concentrations of F^- and Ca^{2+} were fixed to the desired values. Detailed descriptions of simulation and input files can be found in example 1 from Parkhurst and Appelo (Parkhurst and Appelo, 2013a).

Figure S4 shows the Ca^{2+} concentrations and the saturation-index (SI) of CaCO_3 at different pH. The SI of CaCO_3 decreased from ~ 2.3 to -1 as the pH decreased from 11 to 6 indicate that the precipitation of CaCO_3 tend to be formed at high pH and CaCO_3 tend to dissolve at low pH. Accordingly, a lower Ca^{2+} concentration was observed at pH 11.3 and a higher Ca^{2+} concentration was observed at pH 7.

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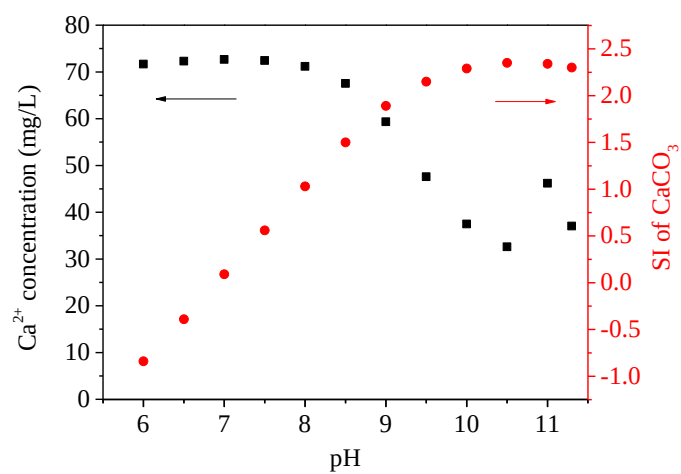


Figure S4. Ca^{2+} concentrations and the saturation-index (SI) of CaCO_3 at different pH.

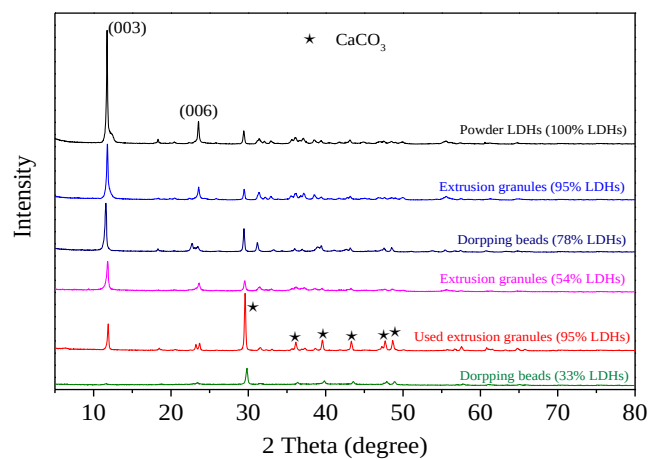


Figure S5. XRD patterns of the powder and granulated Ca-Al-CO_3 LDHs.

Curriculum vitae

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B.Sc. South China Agricultural University (SCAU) Tea Science	Sep.2006-Jun.2010

Experience

Delft University of Technology • Research project on fluoride removal from groundwater	Oct. 2015-Present
University of Chinese Academy of Sciences <i>Graduate Student Research Assistant –Key Laboratory of Aquatic Botany and Watershed Ecology</i> • Analysis of organochlorine pesticides in nine drinking water sources in south China • Design and implement project on OHCs (OCPs, PCBs, PBDEs) in surface water and sediments from East Dongting Lake and Honghu Lake	Sep.2012- Jun.2015
Guangzhou Mingfeng Tea Industry Company <i>Quality Department Manager Assistant, duties included</i> • Tea testing and reports writing	Jul.2010-Aug.2012

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Sep.2006-Jun.2010

Research Assistant– Tea Processing and Machinery Research Laboratory

- Design and implement project on the production and consumption of liquid tea

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Publications

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