

Diseases Prevention by Water Defluoridation Using Hydrotalcites as Decontaminant Materials

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Preventing diseases is deemed to be the major goal of our century especially when an excessive fluoride in drinking water can cause dental fluorosis, bone stiffness, rheumatism and skeletal fluorosis. Fluoride uptake from groundwater implies a worldwide multidisciplinary effort in order to develop renewable, cheap, human friendly materials. Among other materials, hydrotalcites could be good candidates for an efficient fluoride removal from water due to their adsorption, anion exchange and reconstruction properties. These nanostructured materials were synthesized using co-precipitation method in controlled conditions. Presence of anions in the interlayer structure and morphological aspects were performed by FTIR and SEM techniques. Thermal treatment of hydrotalcites showed good adsorption capacities for water defluoridation mostly due to their tendency to restore the original structure.

Keywords: hydrotalcites, fluoride, groundwater, FTIR, SEM

Fluoride releases into the groundwater by slow dissolution of fluorine-containing rocks such as granite, basalt, syenite, and shale and consumption of the contaminated groundwater is the major route of human exposure. In addition, various industries involved in glass and ceramic production, semiconductor manufacturing, electroplating, coal fired power stations, beryllium extraction plants, brick and iron works, and aluminium smelters can add up the fluoride burden in groundwater [1, 2].

Small amounts of fluoride in drinking water are considered beneficial on the dental caries occurrence. Therefore, fluoride is considered harmless for human health at concentration up to 0.7 mg·L⁻¹ and can be dangerous if the concentration exceeds 1.5 mg·L⁻¹ according to World Health Organization [3]. There are countries like China, India, Sri Lanka and South Africa where in some areas fluoride concentrations in groundwater can reach to 30 mg L⁻¹ [4].

Some reports indicated that fluoride may interfere with DNA synthesis. The excess concentrations of fluoride can also interfere with carbohydrates, lipids, proteins, vitamins and mineral metabolism. Fluoride toxicity may occur by several ways. While ingested, fluoride initially acts locally on the intestinal mucosa, it can later form hydrofluoric acid in the stomach, which leads to gastro-intestinal irritation or corrosive effects. Following ingestion, the gastro-intestinal tract is the earliest and most commonly affected organ system. Fluoride can also interfere with a number of enzymes disrupting oxidative phosphorylation, glycolysis, coagulation, and neurotransmission. It is well recognized that individuals with kidney disease have a heightened susceptibility to the cumulative toxic effects of fluoride. In addition, fluoride has been shown to poison kidney function at high doses over short-term exposures in both animals and humans. It has also been concluded by several research groups that fluoride has the ability to interfere with the functions of the brain and pineal gland. Pineal gland is a major site of fluoride accumulation within the body, with higher concentrations of fluoride than either teeth or bone. Fluoride exposure has also been linked to bladder

cancer-particularly among workers exposed to excess fluoride in the workplace. Thyroid activity is also known to be influenced by fluoride. Keeping the view of toxic effects of fluoride on human health, there is an urgent need to find out an effective and robust technology and also efficient materials for the removal of excess fluoride from drinking water [2].

Layered double hydroxides, whose structure and properties were studied extensively, both synthetic and natural origin, belong to a general class called hydrotalcite like compounds or, more generally, anionic clays. Substituted layered double hydroxides result in the occurrence of more synthetic nanomaterials which exploit their further application in various scopes. LDH is a family of two-dimensional anionic clays with the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]A^{n-}_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are di- and trivalent cations, respectively; the value of the coefficient x is equal to the molar ratio of $M^{3+}/(M^{2+} + M^{3+})$; and A^{n-} is an anion. LDH and their calcination products have been successfully employed as adsorbent materials for a variety of anion species and/or pollutants, including sulfur oxides, sodium dodecylsulfate, synthetic dyes, and pesticides. Based on the structure and intercalation characters of LDH, there are three kinds of uptaking mechanisms presented: surface adsorption, interlayer anion exchange, and reconstruction of calcined LDH by the *memory effect*. Considering the di- and trivalent metal ions on the main layers of LDH could be varied in a wide range without altering the structure.

The typical structure of the $Mg^{2+}/Al^{3+} = 2$ and 3 with $R-3m$ space-group, of which the Al^{3+} exists with highly dispersed form. Both two structures, shown in figure 1 are three laminates as a repeating unit [5]. $Mg-Al$ layered double hydroxides (LDHs) intercalated with NO_3^- ($NO_3^-/Mg-Al$ LDH) and Cl^- ($Cl^-/Mg-Al$ LDH) were found to adsorb fluoride from aqueous solutions [6]. With synthetic wastewater, competitive adsorption characteristics of fluoride and phosphate on calcined $Mg-Al-CO_3$ layered double hydroxides (CLDH) were investigated. The results of X-ray diffraction, Scanning Electron Microscopy with energy-dispersive X-ray analyses, and ATR-FTIR demonstrate that

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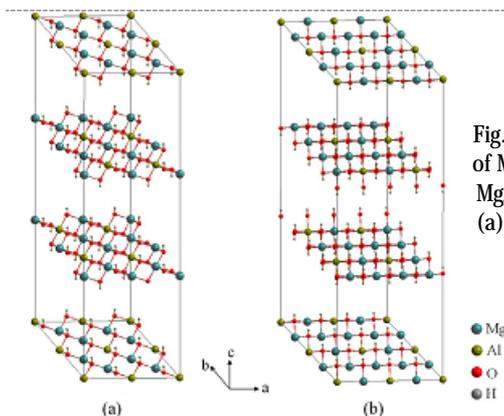


Fig. 1. Sub-lattices of MgAl-LDHs with Mg/Al ratio of two (a) and three (b).

the adsorption mechanism involves the rehydration of mixed metal oxides and concomitant intercalation of fluoride and phosphate ions into the interlayer to reconstruct the initial LDHs structure [7].

Mg-Al oxide obtained by the thermal decomposition of Mg-Al layered double hydroxide (LDH) intercalated with CO_3^{2-} (CO_3 -Mg-Al LDH) was found to take up fluoride from aqueous solution. Fluoride was removed by rehydration of Mg-Al oxide accompanied by combination with F. The Mg-Al oxide after regeneration treatment had excellent properties for removal of F in aqueous solution [8].

A simple ultrasound-assisted co-precipitation method in combination with a calcination treatment was developed to prepare magnetic Mg-Al layered double hydroxides composite as an adsorbent material to remove fluoride ions from aqueous solutions. The application of ultrasound in the preparation process promoted the formation of the hydrotalcite-like phase and drastically shortened the time being required for preparation of the crystalline composite. It was found that the ultrasound irradiation assistance decreased the size of the composite particles and increased the specific surface area, being favorable to the improvement of the adsorption capacity [9].

Nitrate containing Zn-Cr LDHs with Zn/Cr atomic ratio of 2.0, 3.0 and 4.0 were successfully synthesized by co-precipitation. For better practical effectiveness to use these materials in columns, polysulfone/Zn-Cr LDH composite materials with varying the amount of LDHs were prepared by phase inversion technique with an endeavor to increase the aqueous diffusivity. LDHs were found to be stable in the composite beads and gave high efficiency for fluoride removal [10].

Fluoride uptake using various hydrotalcites or derivatives inorganic compounds possessing high defluoridation capacities was reported [11-22]. On the other hand, advanced materials based on organic-inorganic hybrid compounds provided good adsorption capacities for fluoride removal from aqueous solutions [23, 24].

Materials and methods

Synthesis of Mg-Al layered double hydroxides and Zn-Al layered double hydroxides by the direct co-precipitation method:

Mg-Al layered double hydroxides (Mg-Al LDHs) sample was synthesized by co-precipitation method. An aqueous solution obtained by dissolution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0,1 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0,05 mol) as precursor salts in deionized water and a second solution of $\text{NaOH}/\text{Na}_2\text{CO}_3$ were added dropwise together in order to conduct the nucleation process at a pH constant value of 8.5. The resulting slurry was mixed and aged at 60°C for a precise period to perform the aging step. Further, the final precipitate

was filtered, washed two times with deionised water until sodium free and dried at 80°C .

Zn-Al layered double hydroxides (Zn-Al LDHs) sample was obtained the same way using as precursor salts Zn acetate and Al nitrate.

Calcined Mg-Al LDHs and Zn-Al LDHs were obtained by calcining samples in a muffle furnace at 550°C for 5 h.

Characterization of the samples using advanced techniques like FTIR spectra and SEM revealed the presence of anions between sheets and specific morphological features for hydrotalcite type materials.

Water defluoridation experiments

Adsorption studies involved preparation a fluoride solution by dissolving NaF in deionized water. As adsorbent we used 1 g/L hydrotalcite sample in controlled conditions of pH and temperature.

Results and discussions

FTIR analysis

Analytical method FTIR is usually used to identify the type of chemical bonds from a molecule based on IR absorption spectra. Regarding layered structured hydroxides this technique reveals type of anions contained in the interlayer region due to the interactions between incident electromagnetically radiation and electrical dipoles of a molecule.

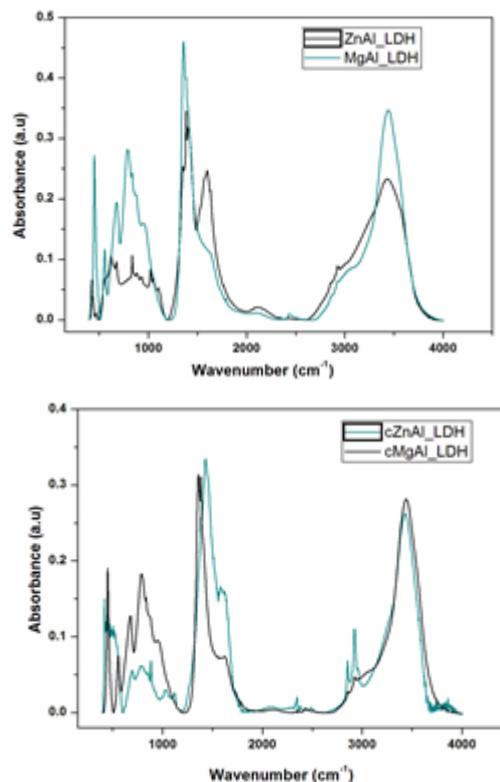


Fig. 2. FTIR spectra of uncalcined (A) and calcined (B) hydrotalcites samples

For both uncalcined samples, first peak around 3500 cm^{-1} can be attributed to the OH groups stretching caused by the interlayer water molecules and hydroxyl groups belonging to metals in hydrotalcite layers. The adsorption bands at 1650 cm^{-1} is specific to bending vibration of the interlayer water. The peak at 1390 cm^{-1} is assigned to carbonate groups. Band area ranging from 400 to 800 cm^{-1} belongs to stretching bands of magnesium and aluminium and zinc and aluminium oxides, respectively. After calcinations the band of hydroxyl and carbonate groups was weakened.

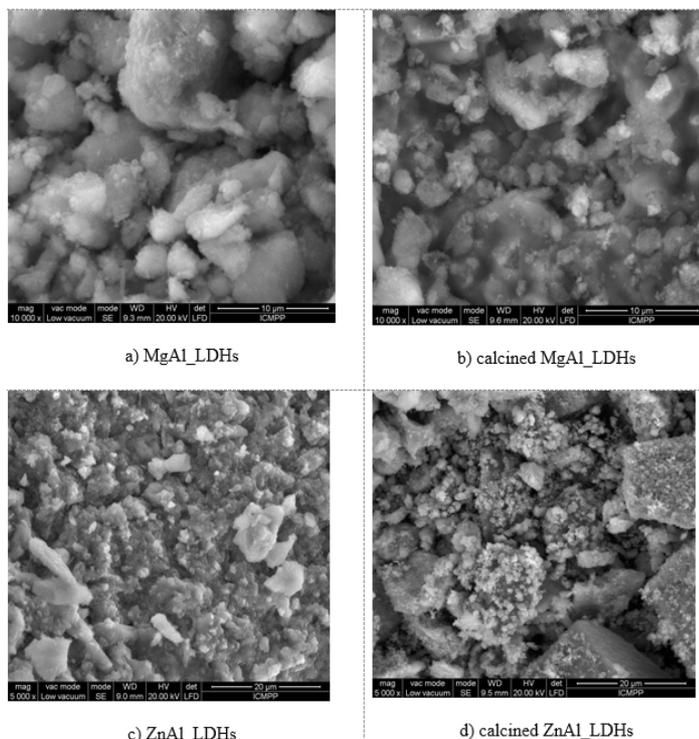


Fig.3. SEM images of a) MgAl LDHs; b) calcined MgAl LDHs; c) ZnAl LDHs; d) calcined ZnAl LDHs

SEM images

Morphological and porosity features shown in Scanning electron microscopy images revealed plate-like particles of MgAl LDHs (fig. 3). Size nanoparticles and agglomeration degree depends on synthesis conditions thus varying shape and size the same as lateral dimension and thickness.

When mixed oxides emerged after calcinations at 550°C it can be seen that plate-like appearance still exists leading to the idea that this process does not change significantly the primary particle morphology.

Furthermore, SEM analysis confirm exhibition of platelet particles morphology for Zn-Al LDHs and calcined Zn-Al LDHs samples.

Adsorption studies

Fluoride removal experiments were performed in 200 mL volume flasks at 25°C under vigorous stirring for 20 h. As adsorbent was used 1g/L of synthesised and thermal treated samples which was added to a 6 mg/L of NaF solution. After 20h the slurry was centrifuged and the supernatant was filtered. UV-Vis spectrophotometer measurements were conducted to determine the amount of fluoride in the filtrate meaning the amount of fluoride adsorbed by each sample calculated by difference and expressed as mgF/gLDH.

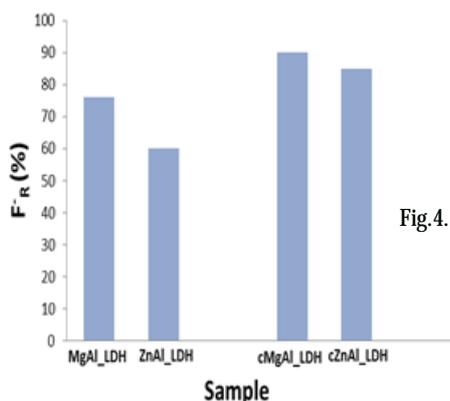


Fig.4. Adsorption rate for samples

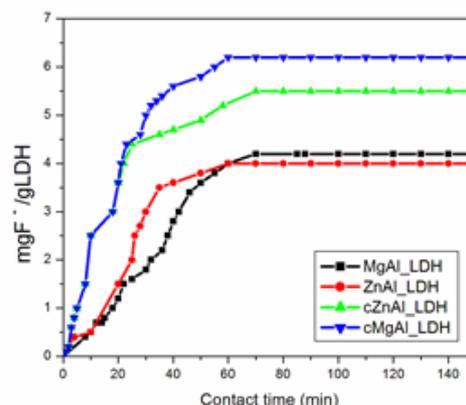


Fig.5. Fluoride adsorption according to contact time

The adsorption capacity of samples in water defluoridation process shown in figure 4 and figure 5 points out that for calcined Mg-Al LDHs sample a maximum adsorption capacity, equal to 92% was reached compared to calcined Zn-Al LDHs sample, equal to 79%. Mixed oxides obtained after thermal treatment showed high adsorption capacities, these materials owning more accentuated porous characteristics. Uncalcined samples revealed lower fluoride removal capacity around 76% for Mg-Al LDHs and 58% for Zn-Al LDHs, respectively. Considering contact time it has been observed that maximum adsorption was registered up to 60 min.

Conclusions

Clear waters represents a major concern regarding diseases prevention caused by accidentally toxic compounds. Researcher's works reported that excessive concentration of naturally or anthropogenic pollutants can cause huge damages for human health.

Regarding uptake of fluoride from groundwater a lot of studies was conducted using cheap, non-toxic, biocompatible, recyclable, naturally or easy synthesized materials possessing adsorption capacities.

Hydrotalcite type materials were synthesized using direct co-precipitation method in controlled conditions of Mg/Al and Zn/Al ratio, pH and temperature that influenced adsorption rate. FTIR spectra and SEM images showed typically features of the agglomerated ensembles of nanoparticles type LDHs and calcined ones.

Higher adsorption capacities was found for calcined samples knowing that the layered structure shrinks at high temperatures with the occurrence of better porosity and uniform pore size distribution. The different pH values, the distinct nature and electro-negativities of the ions present in the synthesis medium, and the different concentrations of the starting solutions could be important factors to control the morphology, to determine the changes of the textural properties and thus make these materials good candidates for water defluoridation.

Experimental results open new perspectives to develop ecofriendly materials for water decontamination thereby to prevent serious diseases.

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