



## Research article

## Defluoridation of groundwater by calcined Mg/Al layered double hydroxide


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## ARTICLE INFO

## Article history:

Received 15 October 2015

Received in revised form

11 January 2016

Accepted 3 March 2016

Available online 25 March 2016

## Keywords:

Fluoride removal

Groundwater

Layered double hydroxide

Drinking water quality

## ABSTRACT

The present study evaluated calcined Mg/Al layered double hydroxide (CLDH) availability for the removal of fluoride from local groundwaters. The Mg/Al layered double hydroxide (LDH) was synthesized by co-precipitation method and characterized by XRD, FT-IR and TGA-TDA analyses. Batch defluoridation experiments were performed under various conditions such as calcination, solution pH, contact time, temperature, material dosage and reuse. Experimental results indicate that fluoride removal strongly increased after calcination of the LDH up to 600 °C. The maximum fluoride removal was obtained at solution pH of 6.85. Kinetics of fluoride removal followed the pseudo-second order kinetic model. The rise in solution temperature strongly enhances the removal efficiency. The adsorption mechanism involved surface adsorption, ion exchange interaction and original LDH structure reconstruction by rehydration of mixed metal oxides and concomitant intercalation of fluoride ions into the interlayer region. The optimum dosages required to meet the national standard for drinking water quality were found to be 0.29 and 0.8 g/L, respectively, for Bejaad and Settat groundwaters. A decrease in the fluoride uptake with increasing the number of regeneration cycles was observed.

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## 1. Introduction

Quality of drinking water is a big challenge in modern days due to the increase in contamination of water bodies. Fluoride is one such contaminant that threatens living organisms, in particular humans. Fluoride is although essential in small quantities for the growth of dental and bones in mammals, but excessive intake of it through foods and drinks cause's dental and skeletal fluorosis [1]. Groundwaters contaminated with excess fluoride is hazardous to health. World Health Organization (WHO) has set a guideline value of fluoride in drinking water at 1.5 mg/L [2].

The fluoride toxicity in groundwater has imposed a serious problem to meet the requirements of drinking water in many countries like India, China, Sri Lanka, Spain, Holland, Italy, Norway and Morocco. Therefore, several technologies have been developed to reduce the amount of fluoride to lower levels from groundwater and other source of waters such as precipitation–coagulation [3], membrane-based processes [4], ion-exchange [5–7], electro dialysis [8] and adsorption processes [9,10].

Layered double hydroxides (LDHs), otherwise referred as hydrotalcite-like compounds are layered materials with general formula  $[M(II)_{1-x}M(III)_x(OH)_2][A_x^{n-}] \cdot mH_2O$ , where M(II) is divalent metal ion, M(III) is trivalent metal ion and A is the anion (may be simple inorganic, organic, or polymers) [11]. In recent years LDHs are widely used as host material to trap anionic pollutants from solutions thus having a good potential in remediation of environmental contaminants. LDHs show high anion exchange capacity and incorporate a wide variety of anions into the inter-layer [12,13]. They have the potential to scavenge hazardous anionic contaminants present in water such as nonionic organic pollutants [14], phenols [15], radioactive <sup>131</sup>I [16], selenate/selenite [17], nitrate

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Peer review under responsibility of KeAi Communications Co., Ltd.



[18], phosphate [19] chromate and arsenate (V) ions [20]. However, the adsorption process by using LDH for different inorganic anions, particularly  $F^-$ , has received less attention.

The principal objective of the present work is to study the defluoridation of local ground waters by Mg–Al–CO<sub>3</sub> layered double hydroxide prepared by co-precipitation. The synthesized material was characterized by X-ray powder diffraction (XRD), Fourier transform infrared (FT-IR), thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA). Further removal efficiency of fluoride has been evaluated by taking different relevant parameters into account.

## 2. Experimental

### 2.1. Materials

All the chemicals used in this study are of analytical grade and were used without further purification. Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was purchased from SDS (France). Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, NaOH, Na<sub>2</sub>CO<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>·2H<sub>2</sub>O were obtained from Sigma–Aldrich (Germany). Acetic acid (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, 99–100%) was obtained from Ridel-De Haen. Sodium fluoride (NaF, 99%) was obtained from Panreac.

### 2.2. Preparation of LDH and CLDH

The Mg–Al–CO<sub>3</sub> LDH material was synthesized by the co-precipitation method at room temperature. A solution containing 0.75 M of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.25 M of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O with Mg<sup>2+</sup>/Al<sup>3+</sup> molar ratio of 3 was made in 100 mL of bidistilled water. Another solution was prepared from 2 M of NaOH and 0.2 M of Na<sub>2</sub>CO<sub>3</sub>. These two solutions were added drop-wise to a stirred vessel. The resulting slurry was aged for 2 h at ambient temperature then treated hydrothermally at 80 °C for 48 h. The pH was maintained at 10.0 ± 0.5 by subsequent addition of 1 M NaOH solution. After that, the solid obtained was recovered by filtration, washed several times with bi-distilled water to remove excess of hydroxide, and dried overnight at 60 °C. The final product was named as LDH in this article. The calcined Mg/Al LDH (CLDH) was obtained by heating the original LDH in a muffle furnace at 600 °C for 3 h in an air atmosphere with a heating and cooling rate of 10 °C/min. Both the calcined and uncalcined LDH were ground prior to analysis or use in fluoride removal experiments.

### 2.3. Characterization

Powder XRD patterns of the samples were recorded using a D2-PHASER de BRUKER-AXS diffractometer with Cu K $\alpha$  radiation operated at 30 kV and 10 mA. Scanning was carried out from 5 to 80° (2 $\theta$ ) at a scan rate of 1°/min and was analyzed using software provided with the instrument. Fourier transfer infrared (FTIR) spectra were recorded on a SCOTTECH SP-1 FTIR instrument. The sample was mixed with oven dried spectroscopic grade KBr and pressed into a disc. The spectrum was recorded between 400 and 4000 cm<sup>-1</sup>. Simultaneous thermogravimetric-differential thermal analysis (TGA-DTA) curves were recorded on a SETARAM (SENSY-Sevo) instrument in argon atmosphere in the temperature range 30–700 °C at a heating rate of 10 °C/min.

### 2.4. Defluoridation experiments

Two different groundwater sources were used in this study; Settat groundwater and Bejaad groundwater. Defluoridation experiments were performed in a series of 100 mL beakers containing the desired weight of each adsorbent and 100 mL of the groundwater. These experiments were carried out at a constant agitation

by varying pH of solution from 4.5 to 10.2, adsorbents dosage from 0.1 to 2 g/L, contact time from 1 to 16 h, and temperature from 10 to 40 °C. The solution pH was adjusted by adding NaOH (1N) or HCl (1N) and measured by a sensION + PH31 pH-meter. The temperature was controlled using a thermostatically controlled incubator. After each defluoridation experiment completed, the solid phase was separated from the liquid phase by centrifugation at 3000 rpm for 10 min and the residual concentration of fluoride was determined.

### 2.5. Determination of fluoride ions concentration

The concentration of fluoride ions in solutions was determined using a selective electrode for fluoride ions. TISAB II (Total Ionic Strength Adjustment Buffer) was added to the solutions to reduce the variation in the ionic strength in the samples. This buffer contains a chelate, which forms complexes with other ions, such as iron and aluminum that could interfere in the determinations. A calibration curve was obtained using NaF standard solutions with different fluoride concentrations.

## 3. Results and discussion

### 3.1. Characterization

The XRD patterns obtained for the precursor material is presented in Fig. 1. XRD pattern of LDH exhibit the characteristic reflections of layered double hydroxides. The diffraction peaks were indexed to a hexagonal lattice with rhombohedral 3R symmetry [21]. It can be observed from the figure the basal peaks for (003) and (006) planes at 2 $\theta$  values between 7 and 26° and the non basal peaks for (101), (015), (018), (110) and (113) planes at high 2 $\theta$  angle. The obtained basal spacing value, calculated from the mean peak baseline (003), was 7.67 Å. This value was very close to those reported in the literature for intercalation of CO<sub>3</sub><sup>2-</sup> ions in Mg/Al LDH [22]. Remarkable changes are observed for CLDHs. The well-defined diffraction peaks of the parent samples were replaced by broad peaks, thus indicating a poor long-range ordered phase. These broad peaks suggest a nanocrystalline material with very small nanoparticles or even an amorphous phase [23]. Layered structure of the original samples is completely destroyed and replaced only by MgO peaks at 2 $\theta$  of 43.6° and 62.9°. The figure also reveals peaks relating to MgAl<sub>2</sub>O<sub>4</sub> spinel, as it starts crystallise at the relatively high temperatures at which the calcination was carried out.

The FT-IR spectra of LDH and CLDH are shown in Fig. 2. The spectra show absorption bands due to hydroxyl groups, water molecules and Mg–O, Al–O and Mg–O–Al stretching vibrations which are typical of LDH materials and have already been reported in the literature [24]. The broad band observed at 3421 cm<sup>-1</sup> is attributed to the interlayer water molecules, this band become less intense in CLDH sample. The weak band at 1637 cm<sup>-1</sup> is due to the bending vibration of interlayer water molecules in LDH [23,25]. The strong band at 1355 cm<sup>-1</sup> was due to the mode of  $\nu_3$  asymmetric stretching of the carbonate anions as reported in the literature [26–28]. This band becomes weaker in CLDH spectra but does not completely disappearing. It can be indicated that the interlayer anions was removed when calcined at high temperatures and carbonate anions are remaining. Thus, calcination at 600 °C destroys the crystal structure of LDH (as confirmed from the XRD pattern in Fig. 1), but does not cause the complete loss of interlayer carbonate anions and bound water. This is in agreement with previous reports that have pointed out that the complete removal of the anionic species occurs only at temperatures higher than 700 °C [29]. The bands in the range of 500–750 cm<sup>-1</sup> are attributed to Mg–O–Mg, Al–O–Al and Mg–O–Al stretching [24,25].

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