



## Research article

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



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## 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  $[M(II)_{1-x}M(III)_x(OH)_2][A_{x/n}^{n-}] \cdot mH_2O$ , 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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[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– $CO_3$  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.  $Mg(NO_3)_2 \cdot 6H_2O$  was purchased from SDS (France).  $Al(NO_3)_3 \cdot 9H_2O$ , NaOH,  $Na_2CO_3$  and  $C_6H_5Na_3O_7 \cdot 2H_2O$  were obtained from Sigma–Aldrich (Germany). Acetic acid ( $C_2H_4O_2$ , 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– $CO_3$  LDH material was synthesized by the co-precipitation method at room temperature. A solution containing 0.75 M of  $Mg(NO_3)_2 \cdot 6H_2O$  and 0.25 M of  $Al(NO_3)_3 \cdot 9H_2O$  with  $Mg^{2+}/Al^{3+}$  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  $Na_2CO_3$ . 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  $10.0 \pm 0.5$  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  $cm^{-1}$ . 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  $CO_3^{2-}$  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  $MgAl_2O_4$  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  $cm^{-1}$  is attributed to the interlayer water molecules, this band become less intense in CLDH sample. The weak band at 1637  $cm^{-1}$  is due to the bending vibration of interlayer water molecules in LDH [23,25]. The strong band at 1355  $cm^{-1}$  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  $cm^{-1}$  are attributed to Mg–O–Mg, Al–O–Al and Mg–O–Al stretching [24,25].

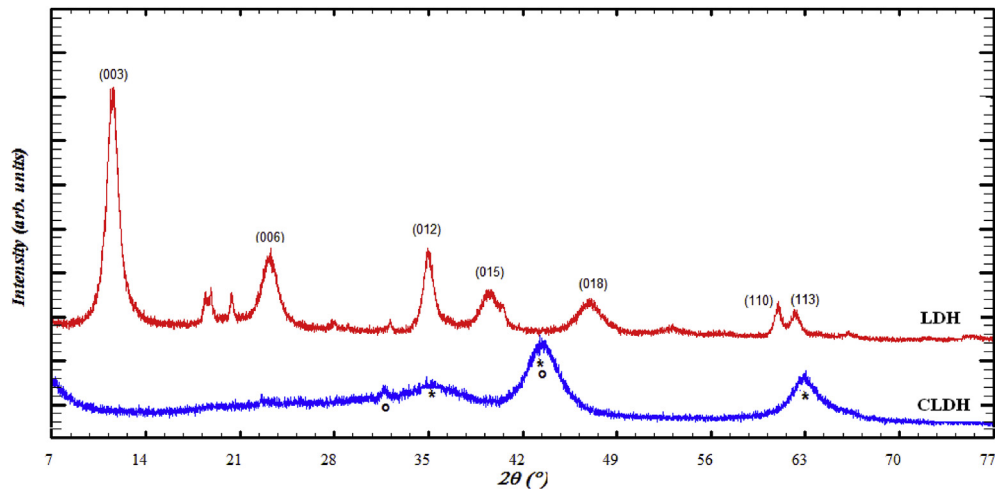


Fig. 1. XRD patterns of LDH and CLDH samples: (\*) MgO and (O)  $MgAl_2O_4$ .

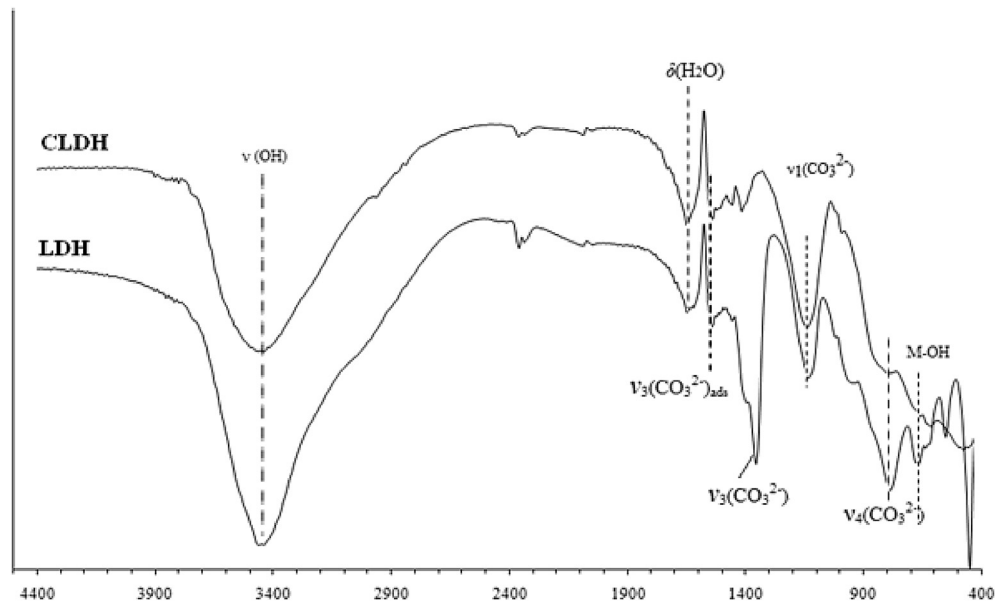


Fig. 2. FTIR spectra of LDH and CLDH samples.

The curves of the thermal analysis (TGA-DTA) showed characteristic profile of Mg–Al–LDH materials (Fig. 3); similar results have been reported by several other authors [30,31]. The TGA curve of LDH shows two steps of thermal decomposition preceded by the loss of adsorbed water around 100 °C. The two steps occur as endothermic processes. The mass loss at 250 was accompanied high change of heat flow. It should be due to the removal of interlayer water. The second distinct mass loss region of 350–460 °C resulted from two processes, the dehydroxylation of the LDH layers and the decomposition of the interlayer  $CO_3^{2-}$  anions. The total mass losses was 34 wt %. The TGA curve of CLDH showed no significant change. The overall loss mass was about 5%, mainly due to moisture, carbonate remained after calcination or adsorbed during storage.

### 3.2. Influence of operating conditions on fluoride removal

#### 3.2.1. Effect of calcination

To find the effect of calcination on fluoride uptake, the materials were heated at 600 °C for 3 h in static air and thus obtained mixed

oxides were assessed for fluoride uptake. The adsorption was carried out by dispersing 0.2 g of LDH or CLDH in 100 mL of Settat groundwater under the condition of pH 6.85, temperature of 30 °C and agitation for 16 h. The percentages of fluoride removal by as-synthesized and calcined LDH are presented in Fig. 4. It can be seen from the figure that the fluoride removal by LDH calcined at 600 °C is highly greater than that of original LDH. This result could be due to two reasons, first, the low anion exchange ability of carbonate ions by fluoride ions in the original LDH. And second, the reconstruction of the LDH structure with the intercalation of  $F^-$  into the CLDH in aqueous solutions. The structure “memory effect” exited in the prepared original layered hydroxide-like structure was reconstructed by intercalation of fluoride into interlayer after adsorption as shown in Fig. 5. The adsorption mechanism in the case of CLDH involved surface adsorption, ion exchange interaction and original LDH structure reconstruction by rehydration of mixed metal oxides and concomitant intercalation of fluoride into the interlayer region [32]. In order to get higher adsorption capacities for fluoride, the CLDH was selected to investigate its adsorption properties in the subsequent experiments.

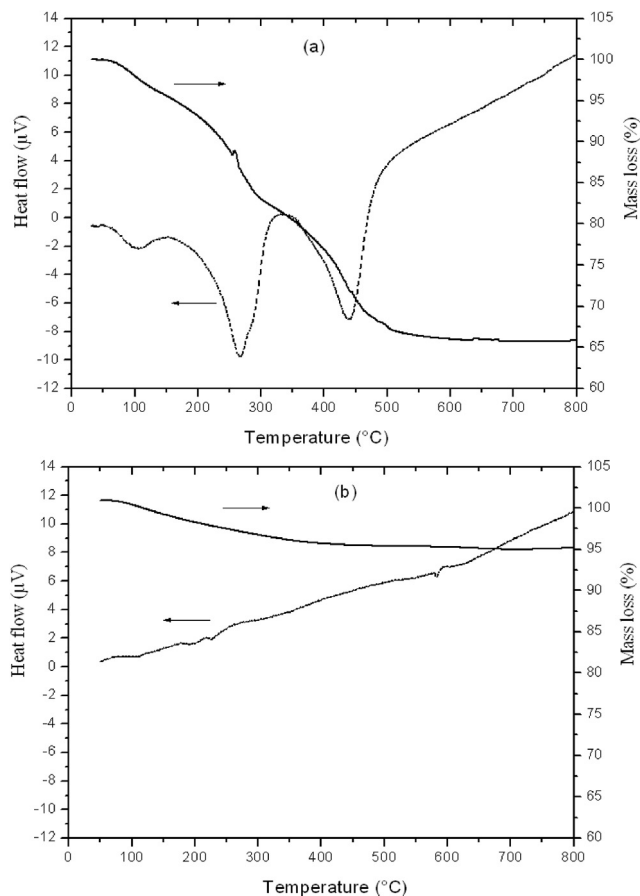


Fig. 3. TGA-DTA curves of LDH (a) and CLDH (b).

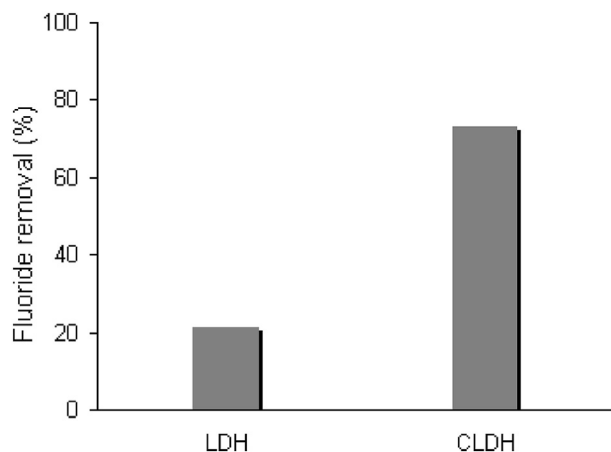


Fig. 4. Fluoride uptake from Settat groundwater over as-synthesized and calcined LDH (material amount = 2 g/L; V = 100 mL; pH = 6, temperature = 30 °C; agitation time = 16 h).

### 3.2.2. Effect of solution pH

The pH is an important parameter to predict the involved mechanism in the process of removing pollutants from wastewater. As presented in Fig. 6, pH had a considerable effect on the removal of fluoride. The fluoride removal increased with increasing solution pH and reached a maximum of 84% at pH of 6.85 before decreasing to 55% at pH of 7.4. The pH values affect the chemistry of both the fluoride ions and the CLDH adsorbent. The effect of pH on fluoride

adsorption can be interpreted by the term of point of zero charge (PZC) of the adsorbents, the pKa of HF as well as the fluoride speciation in solution due to the complex nature of natural groundwaters.

The dissociation constant pKa for HF is 3.17, which means that the fluoride ions exist as anions in solution pH > 3.17. The  $pH_{PZC}$  of the CLDH was found to be 9.6. This means that the surface charge of CLDH was positive when pH < 9.6 and may get negative charges at a solution pH higher than 9.6. According to this result, the pH range used in the experiments should have little impact to the protonation of  $F^-$  and the surface chemistry of CLDH. The sharp change of removal of fluoride observed around pH of 7 could be essentially due to chemical speciation of fluoride in groundwater. Since natural groundwaters contains many species which can bonds with fluoride ions, especially the hardness cations  $Mg^{2+}$  and  $Ca^{2+}$ . Giguère and Campbell demonstrate that fluoride solubility in natural groundwaters is higher at a pH of 7 and is predicted to decrease markedly as a result of fluorite precipitation to  $CaF_2$  and  $MgF_2$  [33]. Similar changes of the adsorption capacity with solution pH have been reported by Mandal and Mayadevi for the adsorption of fluoride ions by Zn/Al layered double hydroxides [34]. Further experiments were conducted at a pH of 6.85.

### 3.2.3. Effect of contact time

Adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. To find an optimum time for the maximum removal of fluoride, uptake studies were carried at different time intervals using 1 g/L ratio of CLDH in 100 mL of Bejaad groundwater. The pH is initially adjusted to 6.85. The obtained result is illustrated in Fig. 7. The figure revealed that the removal takes place in two different steps; the first step was found to be rapid (first 3 h), the second one exhibits a subsequent removal until equilibrium is reached, which is slow and quantitatively insignificant step. Maximum equilibrium uptake was attained within 6 h. Further increase in time had little effect, and hence further studies were carried out for 16 h. In order to characterize the kinetics involved in the fluoride removal process, pseudo-first order and pseudo-second order kinetic models were proposed and the kinetic data were analyzed.

The pseudo-first order rate expression of Lagergren based on solid capacity is generally expressed as follows [35]:

$$q = q_e (1 - e^{-k_1 t}) \quad (1)$$

where  $q_e$  and  $q$  (both in mg/g) are respectively the amounts of fluoride adsorbed at equilibrium and at any time 't', and  $k_1$  (1/min) is the rate constant of adsorption.

The pseudo-second-order model proposed by Ho and McKay [36] was used to explain the sorption kinetics. This model is based on the assumption that the adsorption follows second order chemisorption. The pseudo-second-order model can be expressed as:

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

where  $k_2$  (g/mg min) is the rate constant of pseudo-second order adsorption.

Parameters of the pseudo-first-order and pseudo-second-order kinetic models were estimated with the aid of the non-linear regression. The obtained data and the correlation coefficients,  $r^2$ , are given in Table 1. The table shows that the correlation coefficient for the pseudo-second-order kinetic model is close to unity than

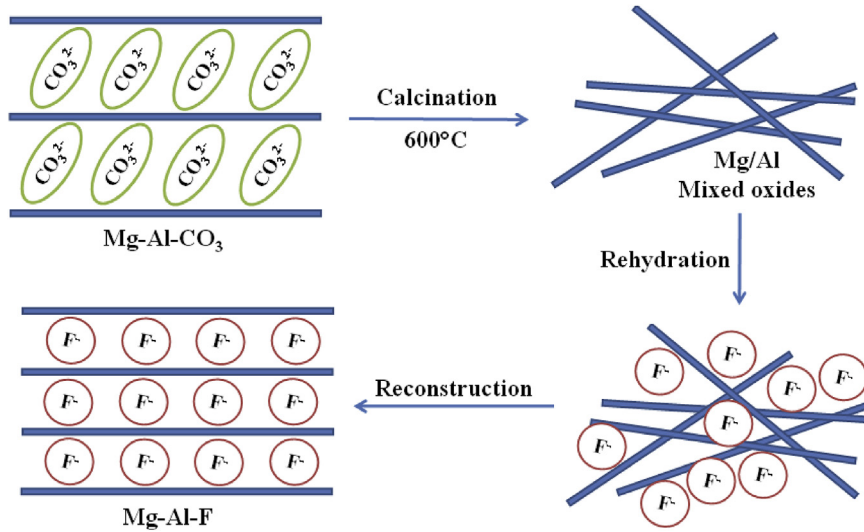


Fig. 5. Schematic illustration of the reconstruction phenomenon of LDH structure.

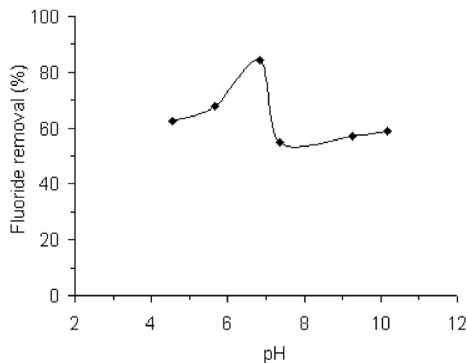


Fig. 6. Effect of solution pH on fluoride removal from Bejaad groundwater by CLDH: ( $V = 100$  mL, material amount = 1 g/L, contact time = 16 h, temperature = 30 °C).

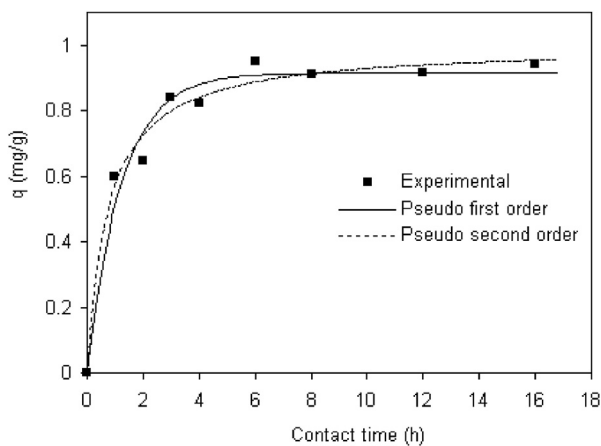


Fig. 7. Kinetics of fluoride removal from Bejaad groundwater by CLDH: ( $V = 100$  mL, material amount = 1 g/L, pH = 6.85, temperature = 30 °C).

that of the pseudo first-order model. Moreover, the calculated value from pseudo second-order model for the amount of fluoride adsorbed at equilibrium ( $q_{cal} = 0.998$  mg/g) were more compatible with the experimental value ( $q_{exp} = 1.014$  mg/g) than the value calculated from the pseudo first-order model ( $q_{cal} = 0.998$  mg/g).

This result suggests that, the removal of fluoride by calcined LDH could be better described by the pseudo-second-order model instead of the pseudo first-order model. Since fluoride adsorption follows pseudo-second order kinetics, this suggested that boundary layer resistance was not the rate limiting step [37]. The rate of fluoride adsorption may be controlled largely by a chemisorption process, in conjunction with the chemical characteristics of the material and fluoride ions.

#### 3.2.4. Effect of temperature

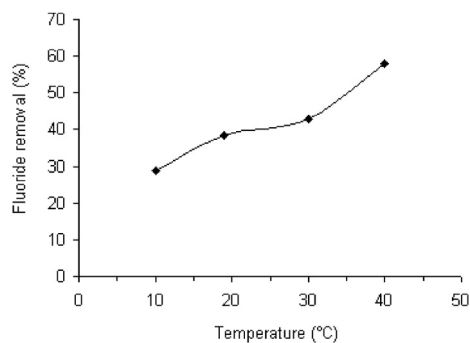
The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbed molecules across the external boundary layer and the internal pores of the adsorbent particles, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [38]. The effect of temperature on fluoride removal from Bejaad groundwater by CLDH is depicted in Fig. 8. The figure indicates that the increase in temperature increases the adsorbed quantities of fluoride ions. The percentage of fluoride removal shows a sharp increase from 28.74% to 57.8% by increasing the temperature from 10 to 40 °C. The result indicates the endothermic nature of the process. The increase in temperature would increase the mobility of fluoride ions as well as produce a swelling effect with in the internal structure of CLDH, thus enabling the fluoride ions to penetrate further [39]. Therefore, the adsorption capacity should largely depend on the chemical interaction between the functional groups on the CLDH surface and the fluoride ions, and should increase as the temperature rises. This can be explained by an increase in the diffusion rate of the fluoride ions into the pores, as diffusion is an endothermic process [40].

#### 3.2.5. Optimization of CLDH dosage

The fluoride removal efficiency from Settat and Bejaad groundwaters with variation of adsorption dose was carried at pH 6.85, temperature (30 °C) and contact time 16 h by varying CLDH dosages from 0.1 to 2.0 g/L. The results are presented in Fig. 9, it can be seen from the figure that the residual concentration sharply decreased with increasing the dosage of CLDH. The observed enhancement in fluoride removal with increasing adsorbent concentration could be due to an increase in the number of possible binding sites of the adsorbent. The optimum dosages required to meet the national

**Table 1**  
Kinetic constants for fluoride adsorption onto CLDH.

$q_{\text{exp}}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
	$q_{\text{cal}}$ (mg/g)	$k_1$ (1/min)	$r^2$	$q_{\text{cal}}$ (mg/g)	$k_2$ (g/mg min)	$r^2$
1.014	0.914	0.813	0.971	0.998	1.335	0.981



**Fig. 8.** Effect of temperature on fluoride removal from Bejaad groundwater: ( $V = 100$  mL, material amount = 1 g/L, pH = 6.85, agitation time = 16 h).

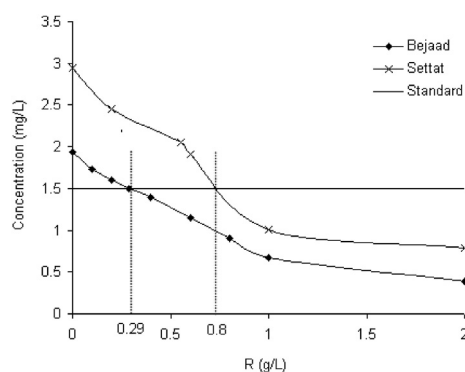
standard for drinking water quality was found to be 0.29 and 0.8 g/L, respectively for Bejaad and Settatt groundwaters. Further studies will be conducted for pilot scale feasibility of this process.

### 3.2.6. Recyclability of the material

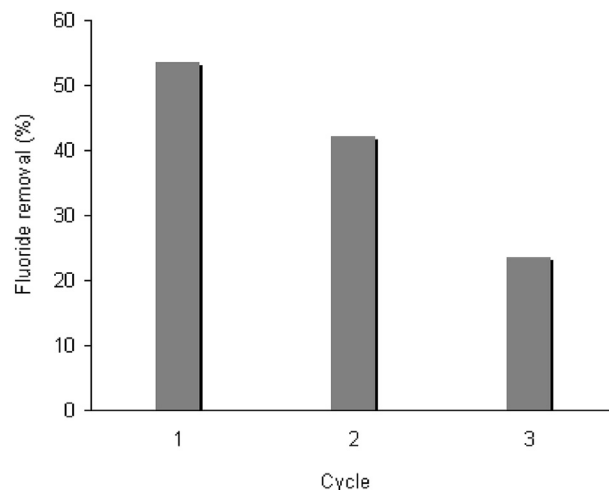
Recyclability of the material discerns its suitability in terms of economic benefit while remediating wastewaters. For regeneration testing, the adsorbent used in the first experiments were recovered by filtration, dried and calcined at 600 °C for 3 h. The above calcined CLDH was then subjected to three successive adsorption–calcination cycles. The obtained results are depicted in Fig. 10. The figure indicates a decrease in the fluoride uptake with an increase the number of regeneration cycles. The fluoride yield in the first cycle was 53% wherein the yield reduced to nearly 23% in the third cycle. The reason for the decrease in the fluoride uptake with cycle is possibly due to the decrease of the crystallinity of the material with the calcination, which is one of the major factors responsible for the reduction of retention capacity. The efficiency of the heat treatment is also a factor to take into account.

## 4. Conclusion

The efficiency of calcined Mg/Al layered double hydroxide, as adsorbent to remove fluoride ions from natural groundwater, has



**Fig. 9.** Variation of fluoride concentration in groundwaters by the increase of CLDH dosage: ( $V = 100$  mL, temperature = 30 °C, pH = 6.85, agitation time = 16 h).



**Fig. 10.** Sequential fluoride removal from Bejaad groundwater over CLDH: (material amount = 1 g/L, pH = 6.85, agitation time = 16 h, temperature = 30 °C).

been studied. It was found that maximum removal of fluoride occurs at pH 6.85. The adsorption process can be well described by the pseudo-second-order kinetic model. The removal yield was strongly enhanced by the rise in temperature. The uptake of fluoride increased with an increase in CLDH loading. The optimum dosages required to meet the national standard for drinking water quality was found to be 0.29 and 0.8 g/L, respectively for Bejaad and Settatt groundwaters. A decrease in the fluoride uptake with an increase the number of regeneration cycles was observed. The results indicate that CLDH is a favorable adsorbent for removal of fluoride from groundwater.

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