

# DEFLOURINATION OF DRINKING WATER USING LAYERED DOUBLE HYDROXIDES

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**Abstract:** Safe drinking water is one of the prerequisites for a healthy life. In Sri Lanka 70% of the population satisfy their water needs from ground water and as a result majority of them suffer from water related problems. One of the pertaining problems prevailing in the dry zone of Sri Lanka is the presence of elevated levels of fluoride ions in drinking water leading to many health related problems. Many studies have been carried out to address the issue however little success has been reported up to date. This study focuses on suggesting a nanotechnology based solution to deflourinate drinking water in the dry zone, Sri Lanka, for domestic water tanks or as a region water purification solution. Layered double hydroxides (LDHs) which readily undergo anion exchange reactions have been used as a suitable candidate for deflourination. The study further concentrates on the regeneration of the material after removal of fluoride ions without releasing fluoride ions back in to the water cycle.

**Keywords:** Deflourination, Layered double hydroxides

## 1 Introduction

An adequate supply of safe drinking water is one of the major prerequisites for a healthy life. Ready access to clean water resources has therefore, become one of the key parameters ensuring that human basic needs are met. About 1 billion people in the world, mostly in developing countries, have no access to potable water while a further 2.6 billion people lacking access to adequate sanitation.[1] Poverty and water are closely linked since it is predominantly the poor who suffers from issues related to water. As a developing country Sri Lanka currently faces a number of water related problems since 70 % of the Sri Lankan population satisfies their water needs from dug wells, deep wells, reservoirs and rivers. [2, 3] One of the pertaining water related problem in the dry zone of Sri Lanka is the presence of elevated levels fluoride ion concentrations as high as 10 ppm in ground water which is well above the WHO recommended levels of 1 ppm. Although fluoride has beneficial effects on teeth at low concentrations in drinking-water, excessive exposure to fluoride in drinking-water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects ranging from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases.[3] Further, it has been reported that chronic kidney disease (CKD) prevalent in the dry zone of Sri Lanka is directly related to the presence of fluoride ions in drinking water.[3] Although, several studies have been carried out to address the problem of excessive fluoride ions in drinking water in dry zone, little success has been reported so far. Most of the reported fluoride removing methods are based on adsorption, precipitation or adsorption/ion-exchange, electro dialysis and electrochemical processes. [4] There are several projects currently operating along with the awareness programmes among the affected communities to introduce different types of treatment methodologies where safe drinking water scarcity prevails due to high fluoride. The most common approach to remove fluoride in the dry zone of Sri Lanka is the use of brick filters which has a low efficiency. [2] In addition a combination of alum (or aluminium chloride) and lime (or sodium aluminate), together with bleaching powder, are added to high-fluoride water, stirred and left to settle. Fluoride is subsequently removed by flocculation, sedimentation and filtration.

Over the past few decades ‘nano’ a little word with big potential has become rapidly insinuating into the world consciousness. Currently, nanotechnology has not left any field untouched and therefore,

this new technology can be harnessed to provide sustainable solutions to water related problems prevailing in Sri Lanka particularly to remove fluoride ions from drinking water.

Layered double hydroxides (LDHs) also known as hydrotalcite like compounds are a class of ionic lamella solids whose layers are positively charged and requires the presence of anions in the inter layer spacing in order to maintain the total charge neutrality. LDHs readily undergo ion-exchange reactions with various anions. High anion exchange capacity and the ability to be regenerated are important factors governing the utility of LDHs as anion exchangers. [5, 6] By utilizing their characteristic ion selectivity, LDHs are expected to find applications in the removal of anion pollutants from liquids particularly for the removal of fluoride ions since the gallery region of an LDH has a high affinity towards fluoride ions. Although, LDHs are rare in nature, they can be readily synthesized by co-precipitating bivalent and trivalent metal salts with a base under controlled conditions in large scales at low cost. [7]

This current study is focused on use of layered double hydroxides as a sustainable method to effectively remove fluoride ions from drinking water in the dry zone of Sri Lanka.

## 2 Objectives and Methodology

The main objective is to develop a cost effective method of domestic or regional defluorination filter using layered double hydroxides.

1. Layered double hydroxides, a synthetic clay material has been successfully used to remove fluoride ions from drinking water in the dry zone, Sri Lanka.
2. A method for regeneration of the filter after saturation has been proposed.

A cost study was performed to determine the cost effectiveness of the system.

All reagents and chemicals used in this study were purchased from the Sigma Aldrich Company, USA and were of analytical grade and used without further purification. All solutions were prepared using distilled water.

### 2.1 Characterization techniques

Powder X-ray Diffraction patterns (PXRD) of all synthesized samples were recorded using a Bruker D8 Focus X-ray powder diffractometer, using Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) over a  $2\theta$  range of  $3-65^\circ$  with a step size of  $0.02^\circ$  and a step time of 1 s.

The chemical nature and molecular bonding of the synthesized samples were determined using Fourier Transform Infra Red Spectroscopy (FTIR), Bruker Vertex80, in a range from  $600$  to  $4000$   $\text{cm}^{-1}$  using Attenuated Total Reflectance (ATR) technique.

### 2.2 Synthesis of Mg-Al-hydroxide LDH (Mg-Al-OH)

Hydroxides intercalated Mg-Al- LDH was prepared by the co-precipitation method. Typically, 100 ml of an aqueous solution containing  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , (Mg:Al = 2:1) was prepared and added drop wise to a 50 ml solution containing hydroxide anion (Al: hydroxide = 1:10) under vigorous stirring conditions. During mixing of the metal solutions, the pH of the reaction mixture was maintained at 10 using 2 M NaOH solution. The solution temperature was maintained at  $25^\circ\text{C}$ , and the reaction was carried out under  $\text{N}_2$  atmosphere. The resulting slurry was aged for 24 hours. The slurry was then filtered, washed three times with distilled water and dried at  $100^\circ\text{C}$ .

### 2.3 Fluoride removal from drinking water using Mg-Al-OH-LDH

To test the fluoride removal capability of LDH, a water sample received from the dry zone, Sri Lanka, which contained 8.2 ppm of fluoride ions was used. First, 0.01 g of LDH was placed in a conical flask. Water containing fluoride ion (100 ml) was poured in to the flask and kept it for 24 hours on the magnetic stirrer. Final concentration of the fluoride solution was tested using an ion selective electrode. Amount of fluoride ions intercalated was calculated by the difference between the initial and final fluoride ion concentrations after stirring for 24 hrs with the synthesized Mg-Al-OH-LDH. Same procedure was carried out varying the weight of the Mg-Al-OH-LDH as 0.05 g, 0.1 g, 0.2 g, 0.5 g, 1 g and 2.5 g in order to build the isotherm for adsorbance.

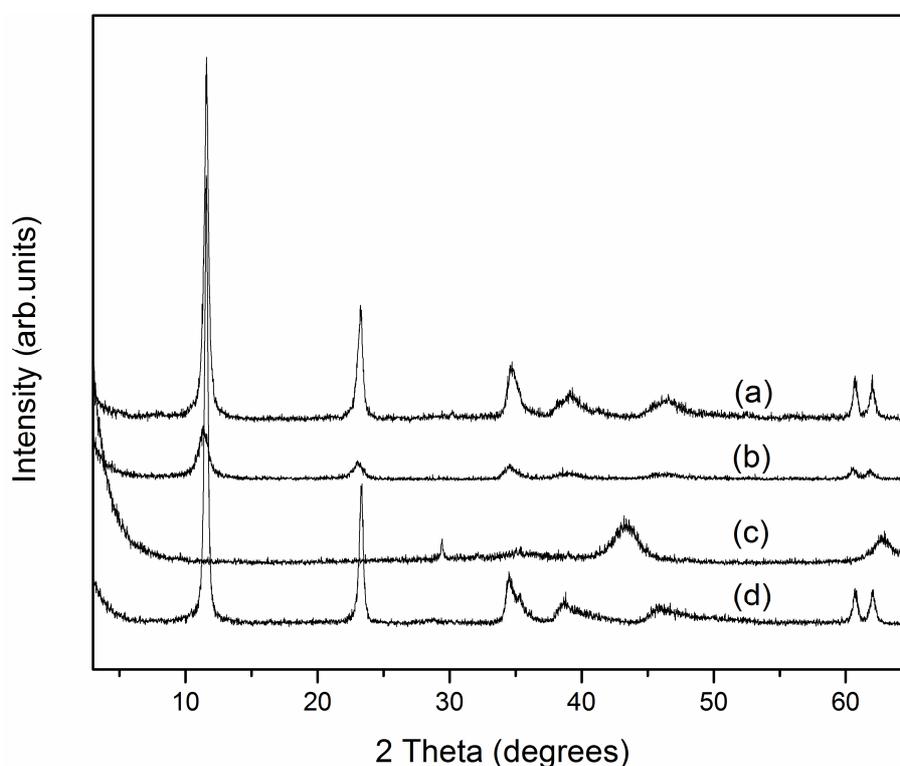
The efficiency of the LDH material was compared with that of the conventional method where brick powder is used as the ion exchange medium.

#### 2.4 Regeneration of the material

Exhausted LDH powder was calcined at 400 °C for three hours. Then the resulting mixed oxide was characterized by PXRD and FTIR. Then it was exposed to 1 M NaOH solution for 24 hours with mechanical stirring and the resulting product was characterized using PXRD and FTIR. The fluoride gas coming out was allowed to absorb into 1 M calcium hydroxide solution.

### 3 Results and Discussion

The parent LDH was characterized using PXRD and FTIR prior to use as a material for removal of fluoride ions from ground water. As depicted by the PXRD pattern of the material (Figure 1(a)) resulting from the co-precipitation reaction represents a typical LDH, consisting of relatively sharp and intense basal reflections at low 2θ values.

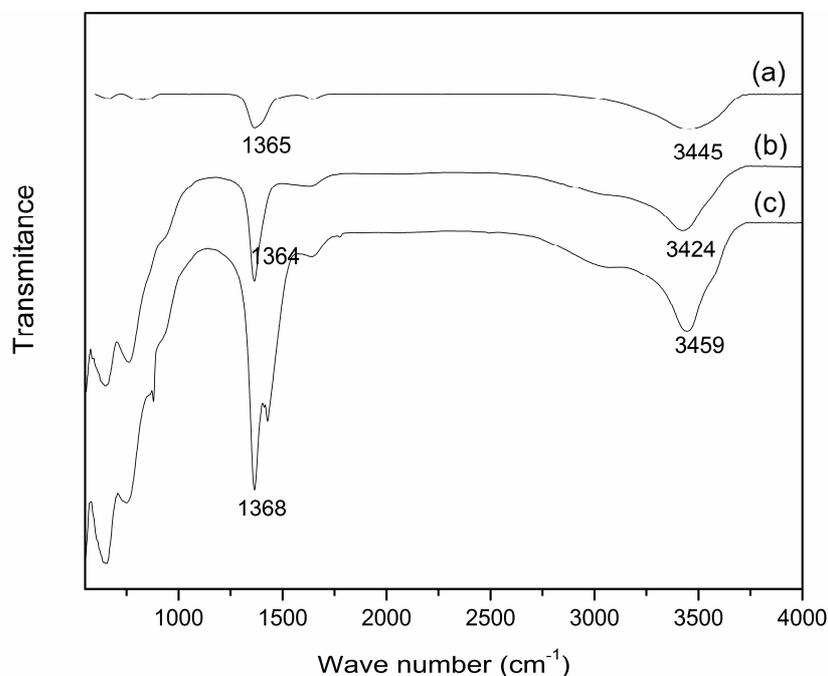


**Fig. 1:** PXRD patterns of (a) Mg-Al-OH LDH, (b) Mg-Al-F LDH, (c) mixed oxide received after calcination of the Mg-Al-F LDH at 450 °C, (d) regenerated mixed oxide in the presence of OH ions.

The main diffraction peaks appear at 11.65°, 23.60°, 34.68° and 60.90° 2 theta are in agreement with the previous reports [5] for hydroxyl intercalated LDHs. According to the Fig 1(a) Mg-Al-OH-LDH exhibits an inter layer spacing of 7.61 nm corresponding to the  $d_{003}$  diffraction peak. The hydroxide ions were selected as the guest ions for the study since they have minimum effect to the drinking water after ion exchange reactions occur.

The parent LDH was further characterized using FTIR techniques in order to understand the nature of functional groups present before and after exposure to fluoride containing ground water. As shown in FTIR spectra (Fig. 2) the main absorption bands are hydroxide stretching, layer hydroxyl bending

motions and the metal-O vibrations of the layers. The very broad band observed around  $3500\text{ cm}^{-1}$  is due to the overlapping stretching modes of hydroxyl groups in the brucite layer and interlayer water molecules. Due to the absorption of small amount of carbonate ions into the interlayer space while the synthesis of Mg-Al-OH LDH, a characteristic band is observed at around  $1360\text{ cm}^{-1}$  which can be assigned to the carbonate stretching vibrations. The bands below  $1000\text{ cm}^{-1}$  are due to M-O vibrations (Mg-O, Al-O) in the brucite layer. [8]



**Fig. 2:** FTIR spectra of (a) Mg-Al-OH LDH, (b) Mg-Al-F LDH, (c) mixed oxide received after calcinations of the Mg-Al-F LDH at  $450\text{ }^{\circ}\text{C}$ .

Then, the hydroxyl ion intercalated LDH was used to remove the fluoride ions from the drinking water obtained from the dry zone, Sri Lanka. The results after removal of fluoride ions are summarized in table 1. As shown in the table an increased efficiency of removal of fluoride ions from drinking water is observed when LDHs are used as the adsorbant, compared with conventional brick powder. The optimum results were obtained when 2.0 g of LDH were used for 100 ml of contaminated ground water.

*Table 1: Fluoride ion concentrations after filtering through LDHs and brick powder.*

Weight of filter material/ (g)	LDH Fluoride concentration (mg/l)	Brick powder Fluoride concentration (mg/l)
0	8.04	8.04
0.01	7.80	7.25
0.05	7.57	6.75
0.1	6.63	6.65
0.2	6.54	6.55
0.5	4.57	6.5
1.0	1.80	5.48
2.0	1.05	5.08

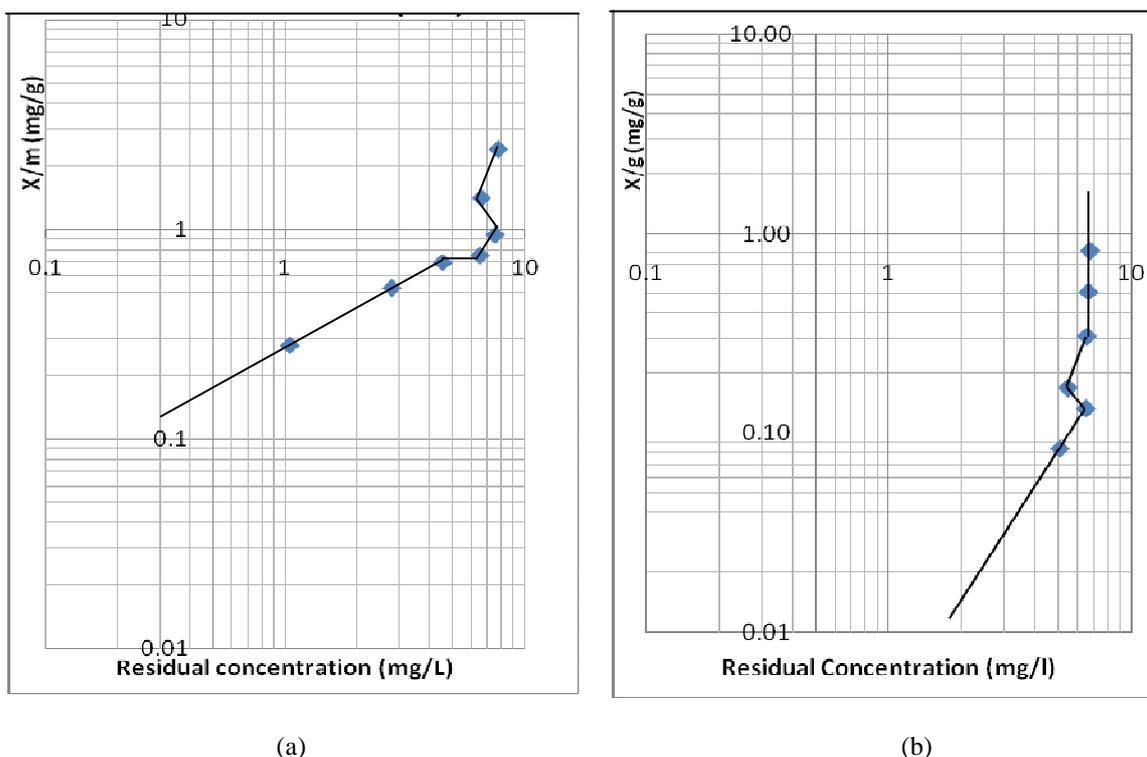
Materials after exposing into the fluoride containing drinking water were characterized by PXRD. According to the figure 1 (b)), the  $d_{003}$  basal spacing of the hydroxyl LDH has shifted to 7.79 nm suggesting a successful absorption of fluoride ions into the LDH galleries. Although both fluoride ions and hydroxide ions have similar affinity for the LDH galleries reaction has occurred by replacing the hydroxide ions possibly via a topotactic mechanism.

As shown in the FTIR spectrum (Figure 2(b)) there is a noticeable shift of the O-H stretching vibrations band from 3445 to 3424  $\text{cm}^{-1}$  due to adsorption of fluoride ions into interlayer spacing of Mg-Al-OH-LDH (Figure 2 (b)). This characteristic shift appears due to the formation of strong H-bonds between intercalated fluoride ions with OH groups present in the LDH.

The isotherm test with different weights of the LDH samples were carried out and compared with that of conventional brick powder (Fig. 3). As given in the figure the fluoride removal capacity of the LDH is much higher than that of the conventional brick powder. Additionally, multi component adsorbance can be observed for the LDH suggesting that other anions impurities in water also can be removed using LDH material. [9]

After saturation of the LDH galleries with fluoride ions regeneration was carried out through calcination process where fluoride removes as a gas. The evolved fluoride ions were absorbed into a  $\text{Ca}(\text{OH})_2$  solution where  $\text{CaF}_2$  is precipitated from the medium.  $\text{CaF}_2$  thus precipitated can be used as an ingredient in the tooth paste industry.

By calcination of Mg-Al-F- LDH, a spinel like solid solution containing MgO and  $\text{Al}_2\text{O}_3$  is obtained at 400  $^\circ\text{C}$  and this solid has a strong Lewis basic character and large specific surface area. These spinels have the ability to recover into the original layered structure, a property known as ‘memory effect’. Therefore, it was possible to recover the hydroxyl intercalated LDH by placing the spinel like mixed oxide with a solution containing hydroxide ions. The regeneration of the Mg-Al-OH LDH was confirmed by comparing the PXRD pattern of the regenerated LDH (Figure 1(d)) and the FTIR spectrum (Figure 2(c)) with the parent material.



**Fig. 3:** Adsorption isotherm for (a) Mg-Al-OH LDH and (b) brick powder.

## 4 Conclusions

Layered double hydroxides have displayed high efficiency in removing fluoride ions from drinking water compared to the methods currently used. LDHs can be used in either regional water purification units or domestic house hold filters. An added advantage of using LDHs would be its superior capability of removing other anions such as carbonate, sulfate which leads to the water hardness.

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## Biographical Sketch

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